Studies in Werner Clathrates. Part 4.[1] Structures of Tetrakis(4-ethylpyridine)di-isothiocyanatonickel(II) and its Clathrates with *p*-, *m*-, and *o*-Xylene, Carbon Disulphide, and Carbon Tetrachloride†

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Two structures of the Werner complex $[Ni(NCS)_2(4Et\text{-}py)_4]$ (4Et-py = 4-ethylpyridine) in its non-porous α phase and the structures of its clathrates with *p*-, *m*-, and *o*-xylene, carbon disulphide, and carbon tetrachloride as the guest molecules have been elucidated. In all the structures the host molecules have octahedral co-ordination and a 'propeller' conformation. The shape and size of a typical cavity has been determined from volume calculations. The packing efficiencies of all structures and the mass spectra of two of the clathrates are discussed.

The separation of aromatic compounds by means of Werner complexes is well known. Remarkable progress in this field was made by Schaeffer *et al.*[2] and by de Radzitzky and Hanotier[3] who managed to achieve fine separations of mixtures of various organic isomers with these host lattices. The host molecules have the general formula MX_2L_4 where M is a bivalent transition-metal cation *e.g.* Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}, and Cu^{II}, X is an anion *e.g.* NCS^-, NCO^-, Cl^-, Br^-, and NO_2^-, and L is an electrically neutral substituted pyridine or α-arylalkylamine. The most versatile and widely studied host complex is $[Ni(NCS)_2(4Me\text{-}py)_4]$ (4Me-py = 4-methylpyridine). Its crystal structures with a wide variety of guest molecules and the physicochemical behaviour of these clathrates have been reviewed by Lipkowski.[4] The thermodynamics of clathration[5] and the scope of application of this complex as the stationary phase in chromatography have been investigated.[6]

Thus far we have synthesised and characterised the structures of $[Ni(NCS)_2(4Me\text{-}py)_4]\cdot MeC_6H_4Pr^i\text{-}p$,[7] $[Ni(NCS)_2(vpy)_4]$ (vpy = 4-vinylpyridine) in the α phase, and its β-phase clathrates with *p*-, *m*-, and *o*-xylenes as guest molecules,[1] $[Ni(NCS)_2(3Me\text{-}py)_4]\cdot CHCl_3$, $[Ni(NCS)_2(4Ph\text{-}py)_4]\cdot 4dmso$ (dmso = dimethyl sulphoxide),[8] and $[Ni(NCS)_2(4Me\text{-}py)_2(4Ph\text{-}py)_2]$ as the host in three clathrate structures where 2-methoxyethanol,[7] 1-chlorobutane, and acetylacetone[9] are the guest molecules. The latter three structures possess channels parallel to a principal crystallographic axis and the length of the guest (*ca.* 10 Å) corresponds closely to that of the corresponding unit-cell parameter, as found in urea inclusion complexes.[10]

We now report two structures of $[Ni(NCS)_2(4Et\text{-}py)_4]$ in its non-porous α phase and as the host in six different clathrates with *p*-, *m*-, and *o*-xylenes, carbon disulphide, and carbon tetrachloride as the guest molecules. Two structures in which the host:guest ratios (Table 1) are different were obtained with carbon tetrachloride as the guest.

Experimental

The 'host' complex in powder form was prepared by treating an aqueous solution of nickel(II) isothiocyanate with a stoicheiometric quantity of 4-ethylpyridine. The resulting fine blue precipitate analysed for $[Ni(NCS)_2(4Et\text{-}py)_4]$. The two types of α-phase crystals of $[Ni(NCS)_2(4Et\text{-}py)_4]$, compounds (**1**) and (**2**), were prepared by dissolving the 'host' powder in tetrahydrofuran [(**1**)] or chloroform [(**2**)] and layering with diethyl ether. Blue needle-shaped crystals grew within 20 h in each case. All clathrates were prepared by initially making saturated solutions of $[Ni(NCS)_2(4Et\text{-}py)_4]$ in the prospective guest liquids. Compound (**3**) was crystallised by layering the saturated solution with diethyl ether; blue octahedrally shaped crystals grew after 24 h. Crystals of compounds (**4**)—(**8**) were grown by slow evaporation from the saturated solutions. All were blue and octahedrally shaped except for those of compound (**8**) which were blue and plate-shaped.

Crystallography.—Single crystals were selected for all structural determinations. The stable α-phase crystals, compounds (**1**) and (**2**), were mounted on glass fibres, while the clathrate crystals were sealed in Lindemann capillary tubes with mother-liquor to prevent deterioration in air due to guest desorption.

Density measurements of crystals were obtained using a linear density column containing water and KI solution in the range 1.00—1.40 g cm^{-3}. The column was calibrated with oil droplets of predetermined densities and a single measurement could be obtained in approximately 5 s. This technique[11] was chosen as being the most rapid and most accurate method of measurement for these unstable crystals.

Intensity data collection. All intensity data were collected at 294 K on a Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). Accurate cell parameters were obtained by least-squares analysis of: (*a*) 25 reflections measured in the range $16 < \theta < 17°$ for compounds (**1**)—(**4**), (**6**)—(**8**); (*b*) 25 reflections in the range $12 < \theta < 13°$ for compound (**5**). In all cases, scans were in the ω–2θ mode with a final acceptance limit of 20σ at 20° min^{-1} in ω and a maximum recording time of 40 s. The vertical aperture length was fixed at 4 mm and for each structure: (*i*) the aperture width (mm) was set according to the formula $x + 1.05\tan\theta$; (*ii*) the scan width, $\Delta\omega/°$ was set according to $y + 0.35\tan\theta$. Table 2 lists values of scan width and aperture width for each structure.

For each data collection the intensities of three reference reflections were periodically monitored to check crystal stability. All intensities were corrected for Lorentz and polarisation factors, but empirical absorption corrections were applied only to compounds (**1**)—(**4**), (**6**), and (**8**).[12–14] Crystal data and experimental details are listed in Tables 1 and 2.

Structure solution. All structures were solved by the heavy-atom method and subsequent Fourier difference syntheses, with least-squares refinement of *F* magnitudes, using the SHELX 76

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Crystal data for the host $[Ni(NCS)_2(4Et\text{-}py)_4]$ (**1**) and (**2**) and its clathrates with various guest molecules, (**3**)—(**8**)

Compound	Guest	Host: guest ratio	M_r/ g mol^{-1}	D_m g cm^{-3}	D_c g cm^{-3}	μ-(Mo-K_α)/ cm^{-1}	$F(000)$	Space group	a Å	b Å	c Å	α °	β °	γ °	U/Å^3	Z
(**1**)			603.50	1.23	1.23	7.04	1 272	$P\bar{1}$	10.359(5)	16.912(5)	19.398(8)	85.62(3)	83.83(4)	73.83(3)	3 241.34	4
(**2**)			603.50	1.24	1.23	7.02	1 272	$P\bar{1}$	10.338(2)	16.113(4)	20.038(2)	91.40(1)	90.83(1)	103.30(2)	3 246.63	4
(**3**)	CCl_4	2:1	680.41	1.28	1.28	7.91	2 840	$I4_1/a$	16.738(4)	16.738(4)	25.174(7)	90	90	90	7 052.42	8
(**4**)	*p*-Xylene	1:1	709.67	1.27	1.25	6.09	1 054	$P\bar{1}$	17.425(2)	17.426(3)	17.721(9)	59.49(3)	59.50(3)	61.05(1)	3 777.01	4
(**5**)	*m*-Xylene	1:1	709.67	1.22	1.21	5.90	1 054	$P\bar{1}$	17.63(3)	17.63(3)	17.749(5)	59.75(8)	59.76(8)	60.5(1)	3 898.87	4
(**6**)	*o*-Xylene	1:1	709.67	1.22	1.21	5.93	1 054	$P\bar{1}$	17.61(2)	17.629(3)	17.666(4)	59.92(4)	59.92(7)	60.16(7)	3 878.75	4
(**7**)	CS_2	1:2	755.78	1.38	1.35	8.26	1 576	$P\bar{1}$	17.35(1)	17.36(1)	17.478(6)	59.84(4)	59.79(5)	60.41(6)	3 724.01	4
(**8**)	CCl_4	1:2	911.15	1.39	1.39	9.94	932	$P2_1/c$	9.356(2)	11.325(6)	20.537(4)	90	92.96(2)	90	2 173.00	2

Table 2. Experimental and refinement parameters for the structures

Compound	Crystal dimensions (mm)	θ Range scanned (°)	Average transmission (%)	Crystal stability (%)	Scan width[a]	Aperture width[b]	Total no. of reflections	Total no. observed[c]	No. of variables	R[d]	R'[e]	Weighting scheme, w
(**1**)	0.16 × 0.19 × 0.34	1—25	95.32	1.62	0.53	1.24	11 757	3 170	371	0.0727	0.0727	$(\sigma^2F)^{-1}$
(**2**)	0.50 × 0.16 × 0.25	1—20	96.37	1.61	0.79	1.13	6 275	3 898	371	0.0765	0.0758	$(\sigma^2F)^{-1}$
(**3**)	0.44 × 0.44 × 0.38	1—20	95.90	2.54	0.69	1.12	3 569	2 182	110	0.0726	0.0721	$(\sigma^2F)^{-1}$
(**4**)	0.22 × 0.25 × 0.34	1—20	98.36	1.42	0.84	1.12	7 382	4 829	433	0.0919	0.0919	Unit
(**5**)	0.56 × 0.44 × 0.38	1—20		1.63	0.83	1.11	6 651	4 771	470	0.1048	0.1048	Unit
(**6**)	0.13 × 0.16 × 0.31	1—20	97.39	2.03	0.60	1.13	6 889	4 582	470	0.1054	0.1054	Unit
(**7**)	0.25 × 0.31 × 0.38	1—25		12.05	0.84	1.12	11 877	7 415	458	0.1079	0.1079	Unit
(**8**)	0.25 × 0.63 × 0.38	1—25	95.33	1.49	1.03	1.24	4 156	2 158	137	0.0597	0.0539	$(\sigma^2F)^{-1}$

[a] $\Delta\omega = (y + 0.35\tan\theta)°$. [b] Aperture width = $(x + 1.05\tan\theta)$ mm. [c] $I_{rel} > 2\sigma I_{rel}$. [d] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [e] $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$.

program system.[15] Fractional atomic co-ordinates are given in Tables 3—9.

The structure of compound (**1**) was solved in space group $P\bar{1}$. Diffractometer intensity data revealed extremely weak reflections where $h + k$ is odd, implying repetition of the structure with a period of half that of the true repeat along the *ab* diagonal. From this observation and the presence of four molecules in the unit cell (obtained from the refined cell parameters and the measured density), it was concluded that the nickel positions are related in pairs: x,y,z and $x + \frac{1}{2},y + \frac{1}{2},z$ and the corresponding centrosymmetric positions. This model is consistent with the presence of a peak of height closest to that of the origin at $\frac{1}{2},\frac{1}{2},0$ in the Patterson map.

Analysis of rotation peaks gave four sets of positions for the two unique nickel atoms. An electron-density map phased on one set revealed 35 peaks in chemically reasonable positions. All the remaining atoms were located in successive electron-density maps. In the final refinement the heavy atoms (Ni and S) were treated anisotropically and hydrogen atoms were constrained to be 1.08 Å from their parent carbon atoms, with a common thermal parameter. Compound (**2**) was refined in the same way, but the thermal parameters of all atoms tended to be somewhat higher than those found for compound (**1**).

The clathrate structures were refined in a similar manner with special care being taken over the location of the guest molecules. No hydrogen atoms were inserted for any guest molecule. Compound (**3**) crystallises in the space group $I4_1/a$ and its structure is reported with respect to the second origin choice at $\bar{1}$.[16] The encaged tetrahedrally shaped carbon tetrachloride molecules occupy the cavities of $\bar{4}$ symmetry, *i.e.* Wyckoff position b. Since there are only four of these sites per unit cell a maximum of one guest can be accommodated for every two host molecules. The guest exhibits disorder despite the fact that it matches the cavity symmetry, and the best model adopted for refinement was one in which the central carbon atom sits on the $\bar{4}$ axis with its chlorine atom in two different positions such that the sum of the two site-occupancy factors is 1, the actual factors of *ca.* 0.8 and 0.2 indicating the chlorine atom is 20% disordered. This description is undoubtedly a gross simplification, and its inadequacy is reflected in its apparent pronounced anisotropy (Table 9).

Compounds (**4**)—(**7**) are all $P\bar{1}$ structures with two independent host molecules per asymmetric unit. Their unit-cell parameters are all similar with $a \approx b \approx c \approx 17$ Å and $\alpha \approx \beta \approx \gamma \approx 60°$ (see Table 1 for the exact parameters), and were treated with suspicion. However transformation to the tetragonal *I*-centred cell indicated by the Niggli values did not yield the required equivalences so the triclinic cell was retained. In compound (**4**) the centrosymmetric *p*-xylene guest molecules match the symmetry of the four sites about which they are located (Wyckoff positions c, d, e, and h); hence the atoms are well ordered and yield acceptable bond lengths and angles. Their isotropic thermal parameters remained similar to those found for the aliphatic carbon atoms of the host molecule, but slightly higher than those found for all other non-hydrogen atoms of the host.

The non-centrosymmetric guests, *m*- and *o*-xylene, in compounds (**5**) and (**6**) were also located about Wyckoff positions c, d, e, and h which are all centres of inversion. The mismatch in symmetry between the guest and the cavity in which it is located results in a smearing of the electron density. A difference electron-density map was calculated and contoured but could be interpreted only by invoking disorder. The best model for refinement of compound (**5**) was obtained by allowing two *m*-xylene molecules to match the electron-density map. These molecules were constructed as idealised rigid bodies with the site-occupancy factors of their carbon atoms fixed to 0.5. Compound (**6**) was refined in a similar manner by allowing two idealised *o*-xylene molecules (carbon atoms all with site-occupancy factors of 0.5) to match the

Table 3. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for compound (**1**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni(1)	−216(2)	11 049(1)	2 501(1)	N(12)	637(11)	11 255(6)	1 518(6)
N(11)	−1 139(11)	10 858(7)	3 472(6)	C(12)	1 191(13)	11 356(8)	997(8)
C(11)	−1 623(13)	10 677(8)	3 989(8)	S(12)	1 992(5)	11 534(3)	272(2)
S(11)	−2 343(5)	10 435(3)	4 706(2)	N(131)	−351(10)	9 888(6)	2 224(6)
N(111)	−2 160(10)	11 628(6)	2 143(5)	C(132)	−671(13)	9 765(9)	1 600(7)
C(112)	−2 316(14)	12 310(8)	1 704(6)	C(133)	−809(13)	9 022(9)	1 413(8)
C(113)	−3 510(14)	12 659(8)	1 404(7)	C(134)	−586(16)	8 360(10)	1 894(9)
C(114)	−4 574(14)	12 338(8)	1 536(7)	C(135)	−228(14)	8 461(10)	2 553(8)
C(115)	−4 415(14)	11 649(8)	1 998(7)	C(136)	−125(13)	9 227(9)	2 684(7)
C(116)	−3 229(13)	11 333(8)	2 276(7)	C(137)	−693(20)	7 492(11)	1 665(10)
C(117)	−5 856(14)	12 690(8)	1 213(7)	C(138)	−697(19)	6 933(12)	2 167(10)
C(118)	−5 716(17)	13 162(10)	523(9)	N(141)	1 731(10)	10 460(6)	2 828(6)
N(121)	−72(11)	12 195(6)	2 783(5)	C(142)	2 708(15)	10 006(9)	2 387(8)
C(122)	−1 041(13)	12 707(8)	3 184(7)	C(143)	4 003(16)	9 673(9)	2 550(8)
C(123)	−961(14)	13 430(9)	3 410(7)	C(144)	4 352(16)	9 775(9)	3 228(8)
C(124)	162(16)	13 679(9)	3 224(7)	C(145)	3 344(15)	10 241(8)	3 656(8)
C(125)	1 212(15)	13 186(9)	2 812(7)	C(146)	2 080(14)	10 562(7)	3 459(7)
C(126)	1 028(14)	12 457(8)	2 584(7)	C(147)	5 888(18)	9 415(11)	3 371(10)
C(127)	369(17)	14 497(10)	3 453(8)	C(148)	6 016(24)	8 723(13)	3 669(13)
C(128)	974(17)	14 409(11)	4 097(9)				
Ni(2)	5 209(2)	4 028(1)	7 513(1)	N(22)	3 734(11)	3 747(6)	7 026(6)
N(21)	6 693(11)	4 332(7)	7 976(5)	C(22)	3 185(13)	3 705(8)	6 563(7)
C(21)	7 357(13)	4 664(7)	8 207(6)	S(22)	2 436(5)	3 640(4)	5 886(3)
S(21)	8 281(5)	5 118(3)	8 527(2)	N(231)	4 992(10)	5 134(6)	6 877(5)
N(211)	5 471(11)	2 944(6)	8 159(5)	C(232)	5 019(12)	5 836(8)	7 131(7)
C(212)	6 689(15)	2 533(9)	8 331(7)	C(233)	4 925(12)	6 569(8)	6 750(7)
C(213)	6 940(15)	1 832(9)	8 784(7)	C(234)	4 869(13)	6 586(8)	6 049(7)
C(214)	5 853(16)	1 555(9)	9 057(7)	C(235)	4 802(13)	5 881(8)	5 770(7)
C(215)	4 589(15)	1 970(9)	8 875(7)	C(236)	4 895(13)	5 173(9)	6 192(7)
C(216)	4 435(13)	2 660(8)	8 423(6)	C(237)	4 738(15)	7 365(9)	5 595(8)
C(217)	6 004(16)	795(10)	9 553(8)	C(238)	5 615(18)	7 879(11)	5 786(10)
C(218)	6 855(22)	786(13)	10 102(10)	N(241)	6 704(10)	3 354(6)	6 758(5)
N(221)	3 705(10)	4 682(6)	8 262(5)	C(242)	7 787(14)	3 606(8)	6 511(7)
C(222)	2 502(13)	5 140(7)	8 082(7)	C(243)	8 736(14)	3 183(9)	6 015(7)
C(223)	1 540(13)	5 625(7)	8 544(7)	C(244)	8 612(17)	2 471(10)	5 782(8)
C(224)	1 844(14)	5 660(8)	9 205(7)	C(245)	7 505(15)	2 195(9)	6 055(7)
C(225)	3 070(14)	5 199(8)	9 407(7)	C(246)	6 601(14)	2 646(8)	6 518(7)
C(226)	3 989(13)	4 718(8)	8 922(7)	C(247)	9 681(20)	1 931(12)	5 236(11)
C(227)	972(16)	6 304(10)	9 777(8)	C(248)	10 792(21)	2 092(13)	5 034(11)
C(228)	−193(24)	6 120(16)	9 850(14)				

electron-density map. The isotropic thermal parameters of the guest atoms were considerably higher than those of the host molecules. A final difference electron-density map calculated after the last full-matrix least-squares refinement yielded four small peaks, all less than 1 e Å^{-3}, in the vicinity of the guest molecules. These peaks were accounted for as imperfect modelling of the disordered xylene. The four crystallographically independent guest molecules in both structures were given individual thermal parameters. Considerable disorder is revealed in both cases by the high thermal parameters of the atoms and ethyl carbons as well as by the estimated standard deviations (e.s.d.s) in their final positional parameters. In compounds (**4**), (**5**), and (**7**) a maximum of one guest can be accommodated per host molecule. This was confirmed independently by careful measurement of the crystal densities (Table 1).

In compound (**7**) the eight guest molecules in the unit cell were also located about Wyckoff positions c, d, e, and h, with two carbon disulphide molecules related by the centre of inversion at each site. They were somewhat disordered. Despite the fact that the sulphur atoms were treated anisotropically, their thermal parameters remained considerably higher than those of the non-hydrogen atoms of the host molecules.

Compound (**8**), which crystallises in space group $P2_1/c$, unique axis *b* and cell choice 1 with the origin at $\bar{1}$,[16] constitutes

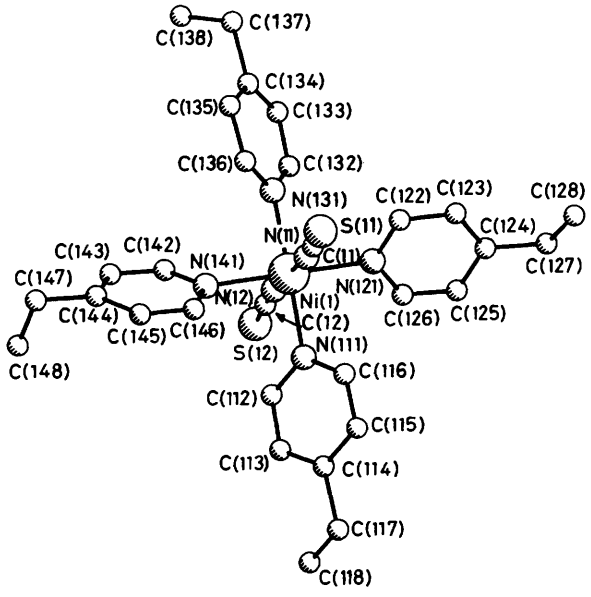

Figure 1. Perspective view of a host molecule of compound (**1**) with the atom numbering

Table 4. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for compound (**2**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ni(1)	700(1)	1 055(1)	7 497(1)	N(12)	2 201(9)	667(6)	8 031(5)
N(11)	−810(9)	1 392(6)	6 962(5)	C(12)	2 826(11)	298(7)	8 249(6)
C(11)	−1 498(12)	1 392(7)	6 527(6)	S(12)	3 713(5)	−260(3)	8 609(3)
S(11)	−2 417(4)	1 414(4)	5 869(2)	N(131)	1 006(9)	2 188(6)	8 104(5)
N(111)	437(8)	−89(6)	6 897(5)	C(132)	−9(12)	2 526(7)	8 258(6)
C(112)	440(10)	−858(7)	7 170(6)	C(133)	140(14)	3 255(8)	8 677(7)
C(113)	322(11)	−1 599(8)	6 790(6)	C(134)	1 382(13)	3 595(8)	8 974(7)
C(114)	169(11)	−1 580(8)	6 116(6)	C(135)	2 394(13)	3 240(8)	8 817(6)
C(115)	133(11)	−832(8)	5 824(7)	C(136)	2 205(12)	2 540(8)	8 383(6)
C(116)	263(11)	−92(8)	6 224(7)	C(137)	1 512(18)	4 480(11)	9 392(9)
C(117)	24(14)	−2 373(9)	5 653(7)	C(138)	1 530(21)	4 224(13)	10 031(10)
C(118)	963(18)	−2 889(10)	5 826(10)	N(141)	−716(9)	402(5)	8 182(5)
N(121)	2 127(8)	1 713(6)	6 821(4)	C(142)	−1 886(11)	−62(7)	7 971(6)
C(122)	3 147(12)	1 403(8)	6 626(6)	C(143)	−2 821(11)	−534(7)	8 390(6)
C(123)	4 047(13)	1 806(8)	6 164(7)	C(144)	−2 574(12)	−508(7)	9 059(6)
C(124)	3 931(15)	2 575(9)	5 892(7)	C(145)	−1 343(12)	16(8)	9 288(7)
C(125)	2 840(13)	2 866(9)	6 089(7)	C(146)	−477(13)	433(8)	8 843(7)
C(126)	1 969(12)	2 436(8)	6 541(6)	C(147)	−3 544(14)	−974(9)	9 548(7)
C(127)	5 180(23)	3 136(14)	5 458(11)	C(148)	−2 982(18)	−1 488(11)	9 994(9)
C(128)	4 831(21)	2 723(14)	4 941(11)				
Ni(2)	4 082(2)	4 070(1)	2 475(1)	N(22)	4 877(9)	3 906(6)	1 552(5)
N(21)	3 253(9)	4 203(6)	3 387(5)	C(22)	5 138(12)	3 783(8)	1 045(7)
C(21)	2 966(11)	4 332(7)	3 895(6)	S(22)	5 497(6)	3 617(4)	278(3)
S(21)	2 568(5)	4 526(3)	4 651(2)	N(231)	3 929(9)	5 312(6)	2 208(5)
N(211)	4 332(9)	2 844(5)	2 752(4)	C(232)	3 719(11)	5 546(8)	1 594(7)
C(212)	5 432(12)	2 598(7)	2 584(6)	C(233)	3 681(11)	6 374(8)	1 429(7)
C(213)	5 696(12)	1 826(8)	2 783(6)	C(234)	3 847(11)	7 000(8)	1 897(7)
C(214)	4 852(12)	1 348(8)	3 190(6)	C(235)	3 998(13)	6 765(9)	2 534(8)
C(215)	3 697(12)	1 568(8)	3 372(6)	C(236)	4 093(13)	5 934(9)	2 678(8)
C(216)	3 476(12)	2 330(7)	3 143(6)	C(237)	3 881(15)	8 013(9)	1 847(8)
C(217)	5 137(15)	503(9)	3 440(8)	C(238)	3 569(22)	8 118(13)	1 207(11)
C(218)	5 817(16)	597(10)	4 090(8)	N(241)	6 009(9)	4 607(6)	2 865(5)
N(221)	2 143(9)	3 509(6)	2 074(5)	C(242)	6 986(12)	5 089(7)	2 484(6)
C(222)	1 917(12)	2 792(8)	1 665(6)	C(243)	8 239(13)	5 365(8)	2 714(7)
C(223)	718(13)	2 460(8)	1 377(7)	C(244)	8 605(13)	5 190(8)	3 351(7)
C(224)	−343(13)	2 829(8)	1 481(7)	C(245)	7 666(12)	4 730(7)	3 726(6)
C(225)	−133(13)	3 540(8)	1 912(7)	C(246)	6 400(12)	4 461(7)	3 491(6)
C(226)	1 090(12)	3 843(8)	2 183(6)	C(247)	10 000(19)	5 520(12)	3 667(10)
C(227)	−1 713(18)	2 535(12)	1 165(10)	C(248)	10 733(25)	6 078(15)	3 491(14)
C(228)	−1 669(22)	2 202(14)	574(14)				

crystallographically a new clathrating phase, the δ phase. The centrosymmetric host molecules were located at Wyckoff position a. The carbon tetrachloride guest molecules are related *via* the centre of symmetry at Wyckoff position c, *i.e.* two guest molecules were located per Wyckoff position c and hence the host: guest ratio is 1:2. For the guest molecules, only the chlorine atoms were treated anisotropically.

All complex neutral atom scattering factors for hydrogen were taken from ref. 17, and for all other atoms from ref. 14, with dispersion corrections from ref. 13. Molecular parameters (Tables) were obtained by use of the program PARST[18] and drawings with PLUTO.[19] All computations were carried out on a Sperry 1100 computer.

Discussion

The host compound, $[Ni(NCS)_2(4Et\text{-}py)_4]$, has thus far proved to be the most versatile in forming Werner clathrates. This diversity is summarised in Table 10 which is adapted from a similar scheme first proposed by Lipkowski.[4]

Compounds (**1**) (Figure 1) and (**2**) are two slightly different α phases which crystallised from different solvents without entrapping guest molecules. The essential difference between the two structures is in the orientation of some of the ethyl groups,

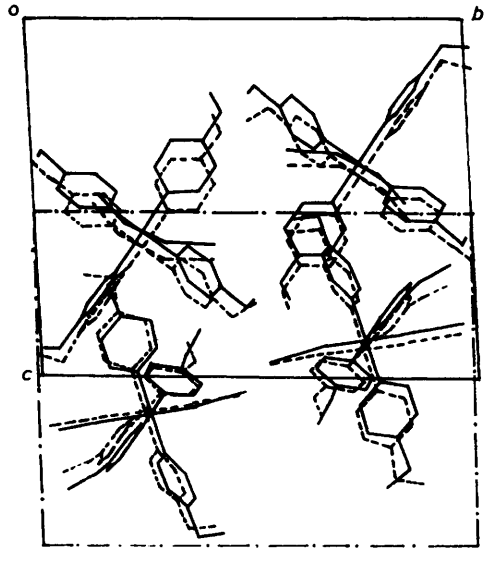

Figure 2. Comparative view of the unit cells of the two α-phase compounds: ——, (**1**) viewed down *a*; – – –, (**2**) viewed down $-a$

Table 5. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for compounds (**3**) and (**8**)

	(3)			(8)		
Atom	*X/a*	*Y/b*	*Z/c*	*X/a*	*Y/b*	*Z/c*
Ni(1)	5 000(0)	2 500(0)	5 541(1)	0	0	0
N(1)	4 062(3)	3 314(3)	5 530(2)	−462(5)	1 302(4)	661(2)
C(1)	3 403(4)	3 483(4)	5 497(2)	−1 027(6)	1 989(5)	971(3)
S(1)	2 467(1)	3 721(2)	5 450(1)	−1 842(2)	2 974(2)	1 390(1)
N(11)	5 573(3)	3 172(3)	6 155(2)	−2 214(5)	−23(5)	−363(2)
C(12)	5 133(4)	3 529(4)	6 522(2)	−2 814(7)	−934(6)	−684(3)
C(13)	5 455(5)	3 894(5)	6 971(3)	−4 147(7)	−866(6)	−1 010(3)
C(14)	6 264(5)	3 882(5)	7 041(3)	−4 921(7)	178(6)	−996(3)
C(15)	6 737(5)	3 530(4)	6 651(3)	−4 318(7)	1 089(6)	−650(3)
C(16)	6 368(4)	3 185(4)	6 217(3)	−2 997(7)	970(6)	−338(3)
C(17)	6 628(6)	4 284(5)	7 533(4)	−6 347(8)	281(7)	−1 376(4)
C(18)	7 100(7)	3 715(7)	7 833(4)	−6 143(11)	743(9)	−2 031(5)
N(21)	4 405(3)	1 839(3)	4 936(2)	−305(5)	−1 322(4)	726(2)
C(22)	4 035(4)	2 212(4)	4 531(2)	21(6)	−1 079(5)	1 353(3)
C(23)	3 687(4)	1 812(4)	4 114(2)	−156(6)	−1 877(6)	1 851(3)
C(24)	3 695(4)	984(4)	4 099(2)	−702(7)	−2 986(6)	1 709(3)
C(25)	4 070(4)	609(4)	4 514(2)	−1 040(7)	−3 252(6)	1 063(3)
C(26)	4 414(3)	1 044(4)	4 920(2)	−815(6)	−2 401(6)	597(3)
C(27)	3 329(4)	509(4)	3 653(3)	−890(7)	−3 890(6)	2 241(3)
C(28)	2 846(5)	974(5)	3 273(3)	−2 409(10)	−4 090(9)	2 379(5)
C(G1)*	0(0)	2 500(0)	6 250(0)	−2 954(8)	4 893(7)	−948(4)
Cl(G1)	379(3)	1 678(4)	6 566(2)	−1 524(2)	5 808(2)	−1 160(1)
Cl(G2)	415(10)	2 896(10)	5 601(7)	−3 087(3)	3 727(2)	−1 500(1)
Cl(G3)				−4 528(3)	5 706(2)	−989(2)
Cl(G4)				−2 583(3)	4 329(2)	−165(1)

* G refers to the guest molecule.

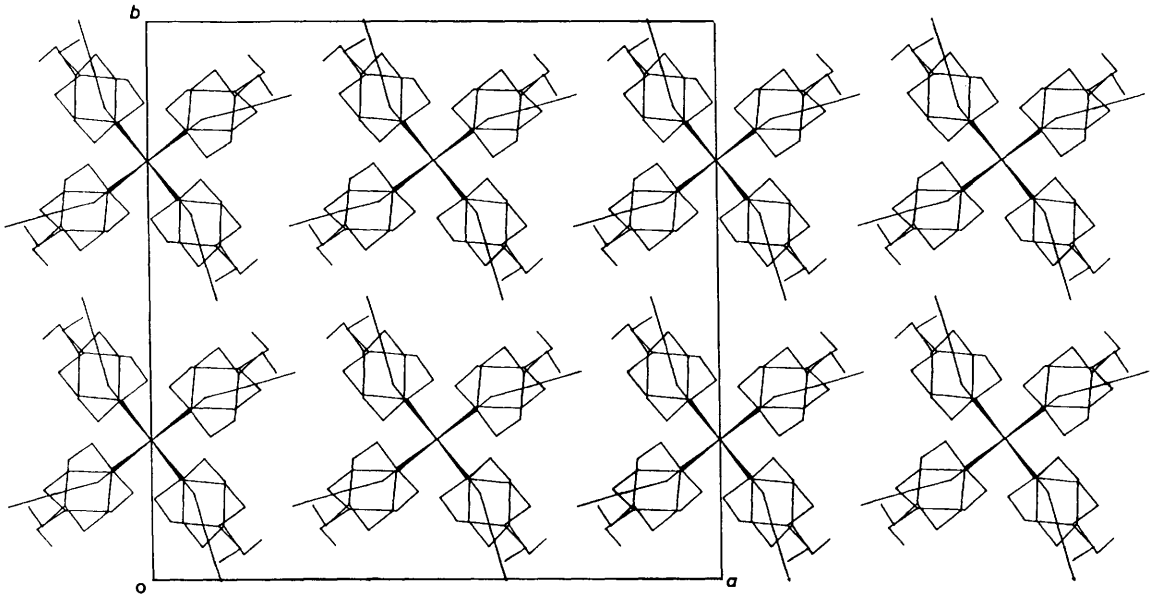

Figure 3. Projection of the β phase [compound (**3**)] down *c*

as shown in Figure 2. The enclathration process requires the α structure to change to a β_0 phase, in which the host molecules have realigned so as to form interstices. This β_0 phase is in turn modified by the entry of guest molecules, into the various clathrate phases β, γ, δ, *etc.* The latter phases arise from the different host : guest ratios and from the varied molecular shapes of the guest molecules.

All the nickel complexes reported here crystallise as mononuclear molecules with each nickel atom co-ordinated to six nitrogen-donor ligands in such a way that they form an irregular octahedron with the isothiocyanates in *trans* positions. The observed bond lengths and angles (Tables 11—14) are within the usual range for compounds of this type. A perspective view of a host molecule [compound (**1**), one of the α

Table 6. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for compound (**4**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni(1)	553(1)	553(1)	1 946(2)	N(12)	1 494(9)	−426(9)	1 295(9)
N(11)	−438(9)	1 490(9)	2 647(9)	C(12)	2 080(11)	−1 019(11)	1 048(11)
C(11)	−1 032(11)	2 075(11)	2 908(11)	S(12)	2 920(4)	−1 880(4)	700(4)
S(11)	−1 879(4)	2 910(4)	3 269(4)	N(131)	742(9)	1 622(9)	621(9)
N(111)	440(8)	−584(8)	3 254(8)	C(132)	1 526(13)	1 491(13)	−112(13)
C(112)	364(11)	−1 377(11)	3 351(11)	C(133)	1 731(13)	2 190(13)	−1 009(13)
C(113)	278(11)	−2 127(12)	4 170(11)	C(134)	1 041(12)	3 059(12)	−1 179(12)
C(114)	268(11)	−2 110(11)	4 950(12)	C(135)	229(12)	3 183(12)	−435(12)
C(115)	345(11)	−1 300(11)	4 838(12)	C(136)	114(11)	2 468(11)	420(12)
C(116)	427(10)	−579(11)	4 013(11)	C(137)	1 216(13)	3 817(14)	−2 143(13)
C(117)	175(14)	−2 928(13)	5 874(13)	C(138)	2 061(15)	4 017(16)	−2 477(16)
C(118)	376(17)	−3 831(15)	5 828(17)	N(141)	1 643(9)	726(9)	2 012(9)
N(121)	−589(8)	431(8)	1 902(9)	C(142)	1 514(13)	1 518(13)	2 078(12)
C(122)	−1 389(11)	373(11)	2 677(11)	C(143)	2 226(13)	1 691(13)	2 088(13)
C(123)	−2 131(11)	280(11)	2 684(11)	C(144)	3 070(12)	1 002(12)	2 072(11)
C(124)	−2 111(11)	253(11)	1 905(11)	C(145)	3 199(12)	227(12)	2 011(11)
C(125)	−1 321(11)	349(11)	1 122(12)	C(146)	2 490(12)	104(12)	1 998(11)
C(126)	−577(11)	423(11)	1 146(11)	C(147)	3 829(13)	1 173(13)	2 112(14)
C(127)	−2 916(13)	159(15)	1 865(14)	C(148)	4 012(17)	2 027(16)	1 372(17)
C(128)	−3 810(15)	351(17)	2 622(16)				
Ni(2)	3 053(1)	3 052(1)	4 449(1)	N(22)	3 701(9)	2 353(9)	5 436(9)
N(21)	2 342(9)	3 705(8)	3 511(9)	C(22)	3 948(11)	2 100(11)	6 043(11)
C(21)	2 091(11)	3 966(11)	2 916(11)	S(22)	4 305(4)	1 733(4)	6 879(4)
S(21)	1 734(4)	4 303(4)	2 086(4)	N(231)	2 982(9)	4 396(9)	4 259(9)
N(211)	3 102(8)	1 751(8)	4 560(8)	C(232)	2 897(12)	5 096(13)	3 489(13)
C(212)	2 342(11)	1 655(11)	4 620(11)	C(233)	2 918(13)	5 991(14)	3 291(14)
C(213)	2 325(12)	818(11)	4 730(11)	C(234)	2 921(12)	6 148(12)	3 984(13)
C(214)	3 095(12)	31(12)	4 750(11)	C(235)	2 983(12)	5 409(12)	4 791(12)
C(215)	3 876(12)	147(12)	4 648(11)	C(236)	2 993(11)	4 575(12)	4 907(12)
C(216)	3 856(11)	977(11)	4 585(11)	C(237)	2 915(13)	7 129(13)	3 800(13)
C(217)	3 135(12)	−902(12)	4 861(14)	C(238)	3 622(16)	7 475(15)	2 924(16)
C(218)	2 415(16)	−827(16)	4 637(17)	N(241)	1 750(8)	3 101(8)	5 585(8)
N(221)	4 393(9)	2 985(9)	3 366(9)	C(242)	1 661(11)	2 331(11)	6 379(11)
C(222)	4 577(12)	2 997(11)	2 545(12)	C(243)	844(11)	2 320(12)	7 123(12)
C(223)	5 424(12)	2 988(11)	1 827(12)	C(244)	44(11)	3 101(11)	7 110(11)
C(224)	6 139(12)	2 914(11)	1 980(12)	C(245)	141(12)	3 887(12)	6 311(11)
C(225)	6 001(13)	2 894(12)	2 816(13)	C(246)	991(11)	3 865(11)	5 567(11)
C(226)	5 117(13)	2 916(12)	3 500(13)	C(247)	−894(13)	3 146(13)	7 900(13)
C(227)	7 082(13)	2 814(13)	1 201(13)	C(248)	−808(16)	2 403(16)	8 798(15)
C(228)	7 392(11)	3 577(10)	990(11)				
C(G11)*	989(15)	4 581(15)	−67(16)	C(G21)	4 565(15)	946(15)	9 530(14)
C(G12)	236(15)	4 299(14)	764(14)	C(G22)	4 301(14)	229(15)	9 704(14)
C(G13)	−690(15)	4 670(15)	848(14)	C(G23)	4 664(14)	−685(14)	10 173(14)
C(G14)	2 003(18)	4 170(17)	−167(18)	C(G24)	4 136(17)	1 972(17)	9 027(17)
C(G31)	5 493(14)	5 047(15)	4 037(15)	C(G41)	4 177(14)	4 821(14)	337(14)
C(G32)	4 721(14)	5 773(14)	5 206(15)	C(G42)	4 242(14)	5 281(14)	718(14)
C(G33)	5 170(14)	5 846(14)	4 326(14)	C(G43)	5 062(15)	5 497(14)	419(15)
C(G34)	5 968(17)	5 168(17)	3 014(17)	C(G44)	5 151(17)	5 995(17)	856(17)

* G refers to the guest molecule.

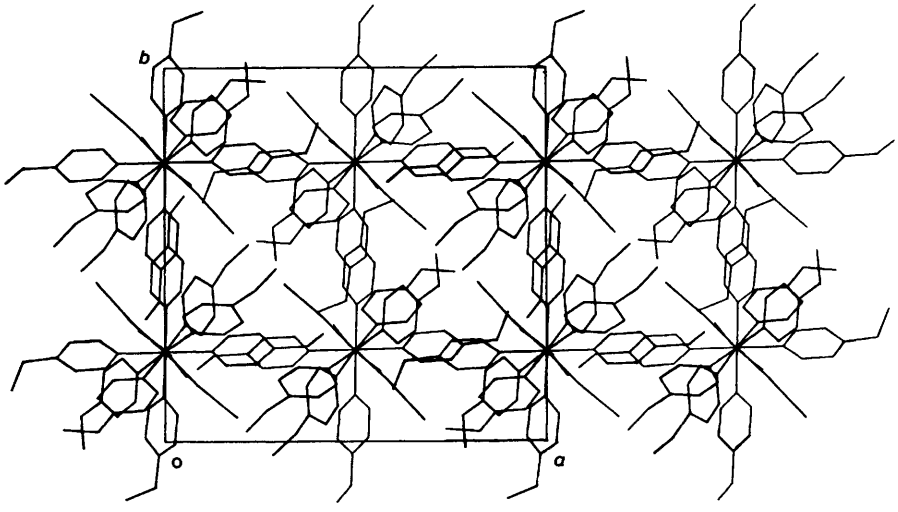

Figure 4. Projection of the pseudo-β phase [compound (**7**) transformed] down *c*

Table 7. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for compound (**5**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni(1)	514(1)	513(1)	1 987(1)	N(12)	1 425(8)	−440(8)	1 316(8)
N(11)	−458(9)	1 436(9)	2 712(9)	C(12)	2 017(10)	−1 041(10)	1 095(10)
C(11)	−1 056(11)	2 031(11)	2 938(11)	S(12)	2 872(4)	−1 890(4)	750(4)
S(11)	−1 891(4)	2 873(4)	3 260(4)	N(131)	658(9)	1 607(8)	668(9)
N(111)	419(8)	−627(8)	3 286(9)	C(132)	1 418(13)	1 507(13)	−10(13)
C(112)	349(10)	−1 385(10)	3 353(11)	C(133)	1 589(13)	2 212(13)	−918(13)
C(113)	283(10)	−2 146(11)	4 170(11)	C(134)	909(12)	3 041(12)	−1 045(12)
C(114)	252(11)	−2 106(12)	4 951(12)	C(135)	122(12)	3 135(12)	−335(12)
C(115)	314(10)	−1 320(11)	4 891(12)	C(136)	6(11)	2 414(14)	522(12)
C(116)	410(10)	−596(11)	4 018(12)	C(137)	1 011(14)	3 837(14)	−1 976(14)
C(117)	152(13)	−2 904(12)	5 920(13)	C(138)	1 903(17)	3 919(18)	−2 443(18)
C(118)	362(15)	−3 790(14)	5 805(16)	N(141)	1 610(9)	660(9)	2 045(9)
N(121)	−623(8)	427(8)	1 906(9)	C(142)	1 515(12)	1 444(13)	2 077(12)
C(122)	−1 390(11)	354(10)	2 682(11)	C(143)	2 192(13)	1 599(13)	2 102(12)
C(123)	−2 133(11)	279(10)	2 678(11)	C(144)	3 034(11)	907(11)	2 092(11)
C(124)	−2 097(11)	250(11)	1 899(12)	C(145)	3 106(12)	121(12)	2 086(11)
C(125)	−1 319(11)	336(10)	1 135(11)	C(146)	2 411(11)	−1(11)	2 035(11)
C(126)	−595(11)	405(10)	1 158(11)	C(147)	3 853(14)	1 020(14)	2 103(15)
C(127)	−2 892(13)	155(13)	1 838(13)	C(148)	3 987(18)	1 889(16)	1 512(18)
C(128)	−3 828(14)	394(16)	2 615(16)				
Ni(2)	3 015(1)	3 012(1)	4 488(1)	N(22)	3 680(9)	2 295(9)	5 438(10)
N(21)	2 307(8)	3 672(8)	3 553(9)	C(22)	3 897(10)	2 081(10)	6 039(12)
C(21)	2 057(10)	3 918(10)	2 965(12)	S(22)	4 244(4)	1 726(4)	6 897(4)
S(21)	1 724(4)	4 249(4)	2 136(4)	N(231)	2 945(9)	4 317(9)	4 350(10)
N(211)	3 097(8)	1 717(8)	4 567(8)	C(232)	2 888(12)	5 043(13)	3 539(14)
C(212)	2 333(11)	1 638(11)	4 637(11)	C(233)	2 685(11)	5 931(14)	3 411(14)
C(213)	2 302(11)	833(10)	4 727(10)	C(234)	2 898(11)	6 050(12)	4 098(13)
C(214)	3 094(12)	48(12)	4 755(12)	C(235)	2 939(11)	5 306(12)	4 890(12)
C(215)	3 885(11)	158(11)	4 661(11)	C(236)	2 954(10)	4 476(11)	5 000(12)
C(216)	3 841(10)	995(10)	4 586(10)	C(237)	2 873(14)	6 993(14)	3 982(14)
C(217)	3 149(12)	−921(12)	4 842(13)	C(238)	3 514(17)	7 405(17)	3 050(16)
C(218)	2 400(16)	−817(15)	4 623(16)	N(241)	1 719(8)	3 087(8)	5 636(8)
N(221)	4 346(9)	2 931(9)	3 381(10)	C(242)	1 663(11)	2 320(11)	6 375(11)
C(222)	4 478(11)	2 952(10)	2 581(12)	C(243)	824(10)	2 307(11)	7 135(11)
C(223)	5 315(12)	2 946(11)	1 856(13)	C(244)	45(11)	3 112(12)	7 102(12)
C(224)	6 041(12)	2 904(11)	1 967(13)	C(245)	134(11)	3 883(11)	6 310(11)
C(225)	5 920(13)	2 872(12)	2 833(14)	C(246)	976(10)	3 845(10)	5 594(11)
C(226)	5 067(14)	2 880(12)	3 492(14)	C(247)	−903(12)	3 149(12)	7 899(12)
C(227)	7 000(14)	2 866(14)	1 172(15)	C(248)	−770(16)	2 385(16)	8 772(15)
C(228)	7 427(18)	3 449(19)	995(19)				
C(G11)*	4 931(20)	4 317(31)	−481(27)	C(G31)	5 386(40)	−246(23)	316(47)
C(G12)	5 803(18)	4 371(28)	−1 061(25)	C(G32)	4 695(34)	−503(19)	399(41)
C(G13)	6 204(18)	4 775(25)	−913(23)	C(G33)	4 147(38)	212(25)	−201(48)
C(G14)	5 748(24)	5 045(39)	−90(40)	C(G34)	4 248(46)	1 099(22)	−750(54)
C(G15)	4 817(22)	5 115(28)	410(27)	C(G35)	4 741(40)	1 358(19)	−576(40)
C(G16)	4 437(22)	4 669(44)	251(37)	C(G36)	5 257(37)	721(28)	72(42)
C(G17)	4 505(24)	4 007(29)	−700(29)	C(G37)	6 083(48)	−949(33)	719(52)
C(G18)	7 181(18)	4 425(28)	−1 199(30)	C(G38)	3 625(32)	−62(35)	−344(40)
C(G21)	4 950(29)	6 002(22)	4 724(21)	C(G41)	−692(19)	5 254(49)	10 038(31)
C(G22)	4 411(32)	5 833(22)	5 665(20)	C(G42)	209(18)	5 273(28)	9 424(19)
C(G23)	4 351(29)	4 956(23)	6 211(19)	C(G43)	910(19)	4 619(47)	9 881(29)
C(G24)	4 723(35)	4 258(20)	5 842(25)	C(G44)	688(26)	4 037(27)	10 840(24)
C(G25)	5 096(34)	4 480(29)	4 871(27)	C(G45)	−218(29)	4 093(28)	11 340(18)
C(G26)	5 230(30)	5 334(24)	4 298(21)	C(G46)	−911(21)	4 662(30)	10 950(21)
C(G27)	4 821(32)	6 926(22)	4 142(25)	C(G47)	−1 429(22)	5 938(30)	9 710(32)
C(G28)	3 821(29)	4 772(28)	7 160(22)	C(G48)	1 795(19)	4 676(32)	9 432(31)

* G refers to the guest molecule.

phases] is shown in Figure 1. This 'propeller' conformation is similar to that of the host molecules found in all the other compounds irrespective of the crystallographic phase.[4]

These clathrated phases are stable only in the presence of guest molecules so the closest one can approximate a β_0 phase is a clathrate containing very small guest molecules. Attempts to crystallise the host powder from methanol, hopefully to entrap these small solvent molecules, always resulted in the formation of an α phase [compound (**1**)]. Lipkowski *et al.*[20] elucidated the structure of $[Ni(NCS)_2(4Me\text{-}py)_4]\cdot 2MeOH$ which must be very close to that of the β_0 phase for $[Ni(NCS)_2(4Me\text{-}py)_4]$.

Compound (**3**) crystallises in the well known β phase, *i.e.* in the space group $I4_1/a$. The host molecules are identical to those found in other β-phase structures.[1,4] However, in all other structures the guest molecules occupy the $\bar{1}$ cavities while in compound (**3**) only the $\bar{4}$ cavities are filled.

Compounds (**4**)—(**7**) all crystallise in the space group $P\bar{1}$, each with four molecules per unit cell. Their triclinic cells are similar and can be related to the β-phase cell by the following transformation. For example, applying the transformation matrix to the triclinic cell of compound (**7**) yields parameters $a' = 17.355$, $b' = 17.377$, $c' = 24.700$ Å, $\alpha = 89.96$, $\beta = 89.97$, and $\gamma = 89.26°$. These are similar to those of the tetragonal cell β structure [compound (**3**)], with $a = 16.738$ and $c = 25.174$ Å. Similar cells can be obtained for compounds (**4**)—(**6**). However the similarity in unit-cell dimensions between the β and pseudo-β phases is not reflected in the relative configurations of the host molecules. This is clearly illustrated in Figures 3 and 4 which

$$\begin{bmatrix} a' \\ b' \\ c' \end{bmatrix}_{\text{pseudo}} \quad \begin{bmatrix} 0 & 1 & -1 \\ 1 & 0 & 0 \\ 1 & -1 & -1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}_{\text{triclinic}}$$

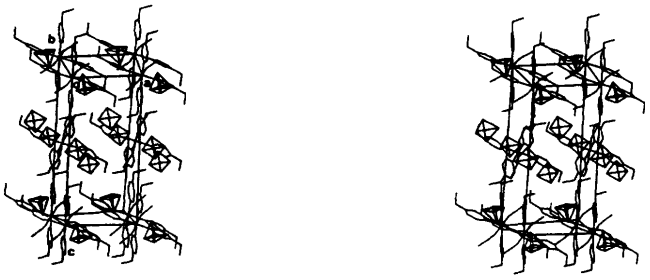

Figure 5. An illustration of the packing of carbon tetrachloride molecules in their cavities in compound (**8**)

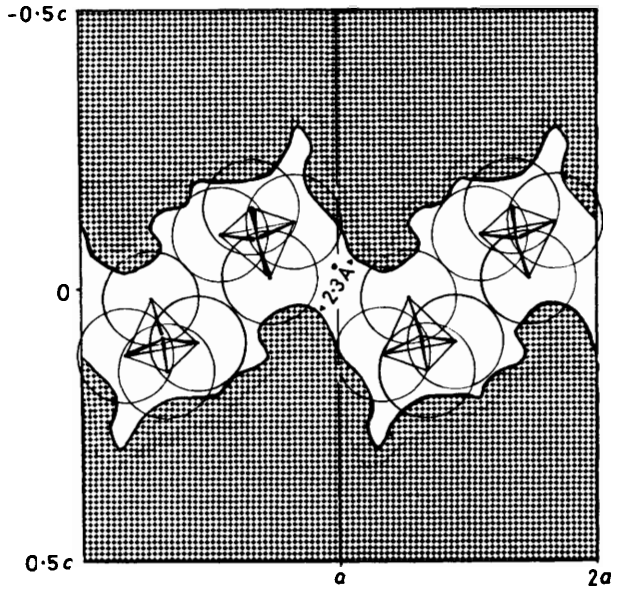

Figure 6. The topology of the channel in two unit cells of compound (**8**) sectioned at $y = \frac{1}{2}$

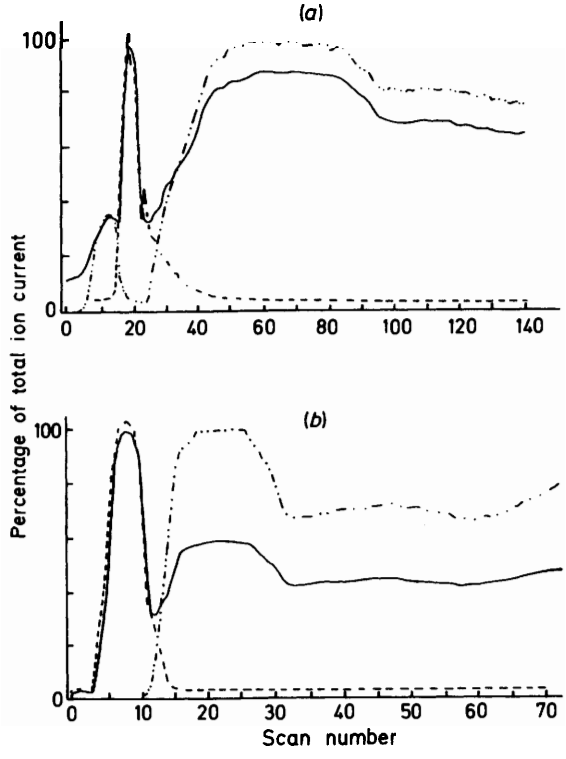

Figure 8. Total-ion-current spectra of compounds (**3**) (*a*) and (**8**) (*b*). – – –, fragment of $m/z = 117$ (guest molecule); — · · —, fragment of $m/z = 107$ (host molecule)

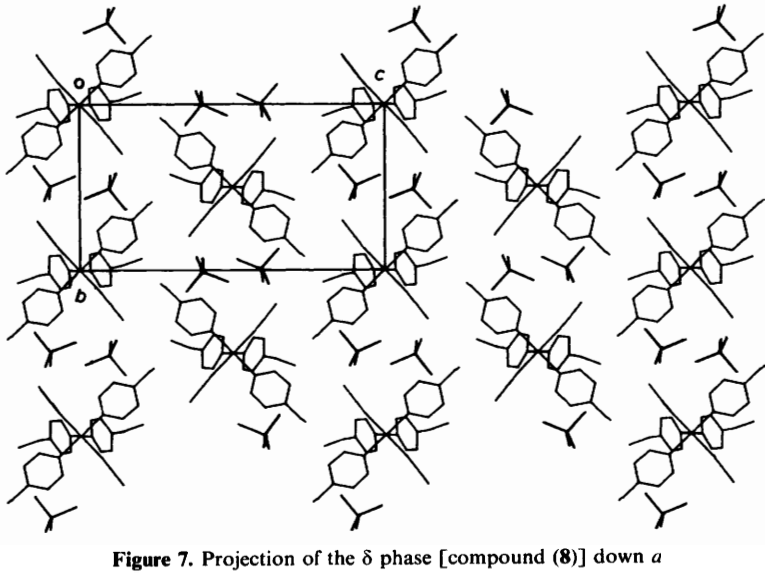

Figure 7. Projection of the δ phase [compound (**8**)] down *a*

Table 8. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for compound (**6**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni(1)	501(1)	501(2)	1 999(2)	N(12)	1 450(9)	−510(10)	2 712(10)
N(11)	−498(10)	1 448(10)	1 358(10)	C(12)	2 047(11)	−1 099(12)	2 950(11)
C(11)	−1 090(11)	2 030(12)	1 101(11)	S(12)	2 843(4)	−1 941(4)	3 322(4)
S(11)	−1 942(4)	2 849(4)	771(5)	N(131)	645(10)	1 578(10)	2 092(9)
N(111)	426(8)	−618(9)	1 940(10)	C(132)	1 424(14)	1 486(15)	2 135(14)
C(112)	350(11)	−1 389(12)	2 670(12)	C(133)	1 618(15)	2 190(15)	2 132(14)
C(113)	274(11)	−2 139(12)	2 693(12)	C(134)	953(14)	3 010(14)	2 076(14)
C(114)	266(11)	−2 138(12)	1 934(13)	C(135)	121(13)	3 142(14)	2 036(13)
C(115)	332(12)	−1 366(13)	1 140(13)	C(136)	8(12)	2 406(13)	2 057(12)
C(116)	408(11)	−622(13)	1 212(13)	C(137)	1 135(15)	3 753(16)	2 096(16)
C(117)	207(15)	−2 969(14)	1 851(15)	C(138)	2 029(16)	3 864(18)	1 415(18)
C(118)	415(18)	−3 840(16)	2 612(18)	N(141)	−645(9)	444(9)	3 280(9)
N(121)	1 589(9)	636(10)	687(9)	C(142)	−1 392(12)	358(11)	3 373(12)
C(122)	1 476(15)	1 442(15)	−33(15)	C(143)	−2 148(12)	295(11)	4 182(12)
C(123)	2 161(15)	1 622(15)	−926(15)	C(144)	−2 149(12)	281(12)	4 948(13)
C(124)	3 013(12)	927(13)	−1 032(13)	C(145)	−1 359(12)	320(12)	4 883(13)
C(125)	3 156(13)	117(13)	−306(13)	C(146)	−608(12)	404(12)	4 008(13)
C(126)	2 426(12)	−20(13)	551(13)	C(147)	−2 924(13)	170(14)	5 901(14)
C(127)	3 772(14)	1 101(15)	−1 992(15)	C(148)	−3 805(15)	360(17)	5 807(17)
C(128)	3 891(18)	1 965(17)	−2 349(17)				
Ni(2)	3 000(2)	3 003(2)	4 499(2)	N(22)	2 291(10)	3 660(10)	5 498(11)
N(21)	3 670(9)	2 280(10)	3 531(11)	C(22)	2 037(11)	3 897(12)	6 094(14)
C(21)	3 900(11)	2 027(12)	2 929(14)	S(22)	1 681(4)	4 223(5)	6 945(4)
S(21)	4 224(4)	1 679(5)	2 152(4)	N(231)	2 919(9)	4 324(10)	3 407(10)
N(211)	3 063(9)	1 732(9)	5 646(9)	C(232)	2 871(14)	5 046(16)	3 534(16)
C(212)	2 326(11)	1 637(12)	6 396(12)	C(233)	2 856(13)	5 913(15)	2 846(15)
C(213)	2 318(12)	816(12)	7 140(12)	C(234)	2 921(12)	6 009(13)	2 001(13)
C(214)	3 089(12)	38(12)	7 137(13)	C(235)	2 944(12)	5 301(13)	1 866(13)
C(215)	3 837(13)	137(13)	6 355(13)	C(236)	2 944(12)	4 473(13)	2 572(13)
C(216)	3 801(12)	965(13)	5 615(13)	C(237)	2 899(16)	6 965(15)	1 250(16)
C(217)	3 139(14)	−887(14)	7 959(14)	C(238)	3 517(19)	7 376(18)	1 103(19)
C(218)	2 362(18)	−798(18)	8 824(17)	N(241)	1 719(8)	3 067(9)	4 566(9)
N(221)	4 303(9)	2 937(9)	4 352(10)	C(242)	1 633(12)	2 321(13)	4 639(12)
C(222)	5 034(14)	2 901(14)	3 539(15)	C(243)	837(12)	2 305(13)	4 706(12)
C(223)	5 925(14)	2 859(12)	3 367(14)	C(244)	50(12)	3 098(13)	4 715(12)
C(224)	6 048(13)	2 898(13)	4 065(14)	C(245)	128(13)	3 847(13)	4 650(12)
C(225)	5 308(12)	2 954(12)	4 871(13)	C(246)	1 001(12)	3 785(13)	4 589(12)
C(226)	4 447(13)	2 957(12)	5 016(13)	C(247)	−921(13)	3 190(14)	4 823(14)
C(227)	6 994(15)	2 894(15)	3 862(15)	C(248)	−846(19)	2 414(18)	4 620(18)
C(228)	7 311(19)	3 569(19)	2 940(19)				
C(G11)*	4 578(31)	4 757(24)	−126(27)	C(G31)	4 662(40)	−160(26)	753(27)
C(G12)	5 193(33)	4 579(21)	274(25)	C(G32)	5 082(33)	424(19)	−140(25)
C(G13)	5 341(34)	5 361(24)	143(29)	C(G33)	5 749(41)	−76(26)	−803(30)
C(G14)	5 131(33)	6 202(21)	−565(29)	C(G34)	5 934(37)	−1 023(27)	−587(32)
C(G15)	4 649(32)	6 314(21)	−1 061(27)	C(G35)	5 451(38)	−1 503(20)	282(36)
C(G16)	4 416(32)	5 586(26)	−891(26)	C(G36)	4 806(36)	−1 081(24)	943(27)
C(G17)	4 392(35)	4 005(28)	4(33)	C(G37)	3 914(37)	287(37)	1 388(29)
C(G18)	5 880(31)	5 226(33)	610(33)	C(G38)	6 140(34)	437(37)	−1 713(26)
C(G21)	3 974(35)	5 185(55)	5 454(28)	C(G41)	−42(22)	4 564(39)	−194(43)
C(G22)	3 904(30)	5 676(41)	4 555(30)	C(G42)	−979(21)	4 801(33)	368(36)
C(G23)	4 760(31)	5 799(36)	3 790(27)	C(G43)	−1 335(20)	5 477(30)	751(33)
C(G24)	5 528(32)	5 608(55)	3 975(33)	C(G44)	−798(26)	5 942(29)	606(37)
C(G25)	5 575(33)	5 074(53)	4 870(45)	C(G45)	165(25)	5 635(38)	166(51)
C(G26)	4 785(35)	4 974(55)	5 639(33)	C(G46)	562(19)	5 043(33)	−431(36)
C(G27)	3 236(36)	4 875(52)	6 258(32)	C(G47)	266(30)	3 805(37)	−489(38)
C(G28)	4 921(43)	5 871(46)	2 882(28)	C(G48)	−2 285(21)	5 762(32)	1 222(35)

* G refers to the guest molecule.

show the packing diagrams of structures (**3**) and (**7**) down their respective *c* and pseudo-*c* axes. This orientation difference in the host molecules prompted the definition of structures (**4**)—(**7**) as a different phase, labelled γ.

Compound (**8**), however, has a quite different stoicheiometry from the chemically similar compound (**3**) and the packing is totally different, as expected owing to the four-fold increase in guest:host ratio. The monoclinic cell dimensions of compound (**8**) cannot be related by any simple transformation to those of any of the other clathrate phases.

A comparison of packing densities for all the compounds was carried out, and the details are listed in Table 15. Interestingly, the α phases [compounds (**1**) and (**2**)] are not as well packed as some of the clathrate phases. This is shown by the high thermal

Table 9. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for compound (7)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ni(1)	537(1)	537(1)	1 965(1)	N(12)	1 462(8)	−425(8)	1 252(9)
N(11)	−444(9)	1 477(9)	2 713(9)	C(12)	2 109(11)	−1 019(11)	1 035(11)
C(11)	−1 020(11)	2 118(12)	2 874(12)	S(12)	3 024(4)	−1 870(4)	736(4)
S(11)	−1 871(4)	3 026(4)	3 111(4)	N(131)	663(8)	1 640(8)	642(8)
N(111)	449(8)	−616(8)	3 256(8)	C(132)	1 486(12)	1 548(12)	−78(12)
C(112)	378(9)	−1 390(9)	3 329(10)	C(133)	1 630(13)	2 258(12)	−963(13)
C(113)	296(10)	−2 175(11)	4 168(11)	C(134)	956(11)	3 074(11)	−1 126(11)
C(114)	278(10)	−2 148(10)	4 974(11)	C(135)	83(11)	3 214(12)	−389(11)
C(115)	332(10)	−1 331(11)	4 873(12)	C(136)	−30(12)	2 457(12)	485(12)
C(116)	423(10)	−606(11)	4 044(11)	C(137)	1 102(15)	3 841(14)	−2 070(15)
C(117)	190(13)	−2 976(12)	5 889(13)	C(138)	1 813(15)	4 234(16)	−2 339(16)
C(118)	310(14)	−3 875(14)	5 874(15)	N(141)	1 639(9)	667(9)	2 054(9)
N(121)	−625(8)	442(8)	1 922(8)	C(142)	1 552(12)	1 483(12)	2 049(12)
C(122)	−1 389(9)	371(9)	2 682(10)	C(143)	2 277(11)	1 632(12)	2 055(11)
C(123)	−2 164(11)	276(10)	2 707(11)	C(144)	3 068(12)	944(12)	2 078(12)
C(124)	−2 148(10)	283(10)	1 896(11)	C(145)	3 212(13)	110(13)	2 069(12)
C(125)	−1 357(10)	352(10)	1 132(11)	C(146)	2 463(11)	−22(12)	2 079(11)
C(126)	−608(11)	418(10)	1 146(11)	C(147)	3 849(15)	1 106(16)	2 109(16)
C(127)	−2 945(12)	175(13)	1 889(13)	C(148)	4 256(17)	1 809(17)	1 242(17)
C(128)	−3 854(14)	305(15)	2 699(14)				
Ni(2)	3 036(1)	3 037(1)	4 466(1)	N(22)	3 717(9)	2 311(9)	5 429(10)
N(21)	2 309(9)	3 722(9)	3 542(10)	C(22)	3 951(13)	2 130(13)	6 008(13)
C(21)	2 125(12)	3 956(13)	2 925(13)	S(22)	4 262(4)	1 889(5)	6 875(4)
S(21)	1 885(4)	4 270(4)	1 967(4)	N(231)	2 959(8)	4 352(8)	4 332(8)
N(211)	3 082(8)	1 741(8)	4 554(8)	C(232)	2 933(12)	5 089(13)	3 515(14)
C(212)	3 850(10)	965(10)	4 577(10)	C(233)	2 910(12)	5 960(12)	3 381(13)
C(213)	3 881(11)	129(11)	4 663(11)	C(234)	2 905(12)	6 120(12)	4 074(13)
C(214)	3 085(11)	44(11)	4 710(11)	C(235)	2 930(11)	5 403(12)	4 901(13)
C(215)	2 294(10)	827(10)	4 703(10)	C(236)	2 924(11)	4 518(11)	5 050(12)
C(216)	2 319(9)	1 674(9)	4 607(9)	C(237)	2 859(15)	7 073(15)	3 930(16)
C(217)	3 105(12)	−887(12)	4 812(13)	C(238)	3 718(15)	7 354(16)	3 188(16)
C(218)	2 311(14)	−866(14)	4 708(15)	N(241)	1 731(8)	3 085(8)	5 618(8)
N(221)	4 341(9)	2 962(8)	3 361(9)	C(242)	1 676(10)	2 323(10)	6 390(10)
C(222)	5 074(12)	2 950(12)	3 466(14)	C(243)	820(10)	2 308(10)	7 159(11)
C(223)	5 972(13)	2 911(12)	2 719(13)	C(244)	56(10)	3 081(10)	7 152(10)
C(224)	6 122(12)	2 889(12)	1 899(12)	C(245)	132(10)	3 888(10)	6 342(10)
C(225)	5 398(12)	2 908(11)	1 785(13)	C(246)	954(9)	3 856(10)	5 609(10)
C(226)	4 507(12)	2 935(11)	2 530(12)	C(247)	−898(12)	3 117(13)	7 963(13)
C(227)	7 095(14)	2 843(12)	1 136(15)	C(248)	−857(15)	2 272(15)	8 877(14)
C(228)	7 330(15)	3 711(15)	741(15)				
C(G1)*	4 120(17)	1 100(19)	9 337(17)	C(G3)	4 342(18)	5 432(17)	6 088(20)
S(G11)	3 977(5)	186(6)	9 597(6)	S(G31)	4 610(6)	6 235(6)	5 163(6)
S(G12)	4 164(7)	2 102(7)	8 942(6)	S(G32)	3 961(6)	4 768(7)	7 090(7)
C(G2)	1 108(20)	4 138(19)	431(17)	C(G4)	4 564(18)	5 653(19)	910(18)
S(G21)	176(6)	3 990(5)	1 211(6)	S(G41)	3 765(6)	5 381(6)	1 012(6)
S(G22)	2 121(7)	4 156(7)	−228(7)	S(G42)	5 232(7)	6 046(6)	825(7)

* G refers to the guest molecule.

parameters, indicating partial disorder, of some carbon atoms (particularly those of the more mobile ethyl groups) in structures (**1**) and (**2**). A more incisive picture, however is obtained by calculating the space available for one guest molecule in each structure. The volume occupied by one host molecule was taken as a constant [averaged from structures (**1**) and (**2**)] at 211.0 Å^3. The sum of the volumes of all the host molecules in the unit cells of the clathrate compounds was subtracted from the unit-cell volumes obtained experimentally and thus the so-called remaining volume per guest molecule can be evaluated. As demonstrated in a previous study,[1] structures (**5**) and (**6**), which contain disordered *m*- and *o*-xylene located about centres of inversion, have a larger guest volume than that of the more ordered *p*-xylene structure, (**4**). Taking the volume of a methyl group to be 23.5 Å^3,[21] the volume differences between disordered and ordered guests correspond to 1.3 and 1.1 methyl groups. This accords well with the disorder model chosen in the final refinement.

Structures (**3**) and (**8**), which contain carbon tetrachloride as the guest, exhibit different modes of enclathration. Gavezzotti's program OPEC[22] was used to map precisely the sizes and shapes of the guest cavities. In compound (**3**) the guest lies in a $\bar{4}$ site and the shape of this site is an approximately spherical cage with a volume of 148 Å^3. According to Kitaigorodski,[21] an ordered carbon tetrachloride molecule occupies 85 Å^3. Considering the partial disorder of the molecule in compound (**3**), this calculation of the cage volume is deemed satisfactory. In contrast, compound (**8**) possesses channels which zigzag along *a* as in Figure 5, where the guest molecules are shown schematically as tetrahedra. The topology of the channel is shown in Figure 6, which displays two unit cells sectioned at $y = 0.5$, where the channel is at its widest. The channel has a

Table 10. A two-dimensional schematic diagram of the enclathration of different guest molecules by $[Ni(NCS)_2(4Et\text{-}py)_4]$

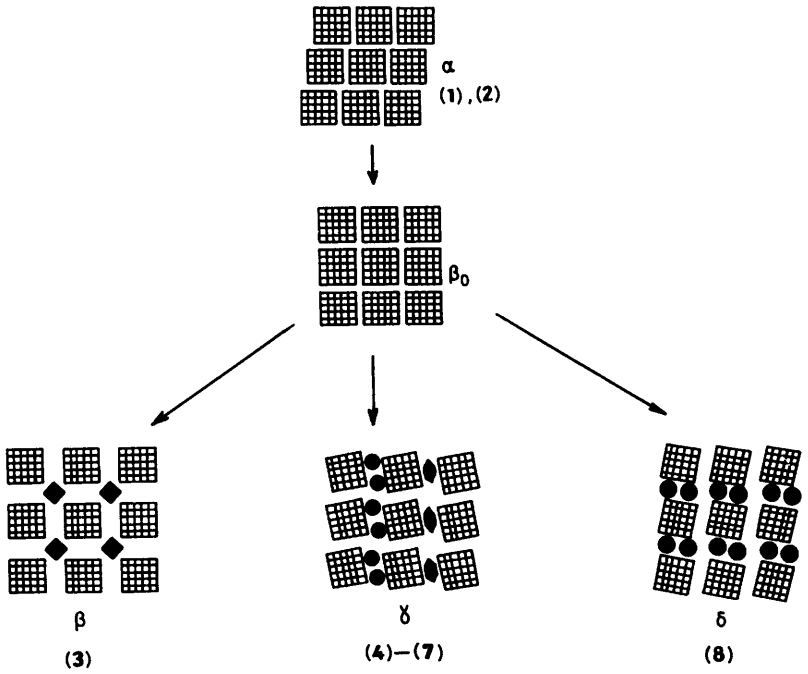

Table 11. Bond distances (Å) with e.s.d.s in parentheses for compounds (1), (2), and (4)—(7)

	(1)	(2)	(4)	(5)	(6)	(7)
Ni(1)–N(11)	2.064(10)	2.062(10)	2.063(12)	2.083(14)	2.081(15)	2.106(7)
Ni(1)–N(12)	2.060(10)	2.093(10)	2.053(12)	2.063(13)	2.111(14)	2.086(6)
Ni(1)–N(111)	2.143(9)	2.139(9)	2.145(10)	2.160(11)	2.100(20)	2.130(6)
Ni(1)–N(121)	2.102(9)	2.132(9)	2.147(11)	2.157(18)	2.138(11)	2.141(6)
Ni(1)–N(131)	2.120(3)	2.127(9)	2.116(11)	2.142(11)	2.125(22)	2.126(6)
Ni(1)–N(141)	2.127(8)	2.134(9)	2.131(11)	2.128(20)	2.141(11)	2.121(6)
Ni(2)–N(21)	2.059(10)	2.055(11)	2.086(12)	2.099(16)	2.148(20)	2.061(7)
Ni(2)–N(22)	2.058(9)	2.071(11)	2.071(12)	2.051(17)	2.100(20)	2.054(7)
Ni(2)–N(211)	2.108(8)	2.135(8)	2.134(10)	2.152(16)	2.141(11)	2.138(6)
Ni(2)–N(221)	2.137(8)	2.136(9)	2.134(11)	2.164(12)	2.133(19)	2.106(6)
Ni(2)–N(231)	2.131(8)	2.124(9)	2.137(11)	2.141(18)	2.149(13)	2.116(6)
Ni(2)–N(241)	2.151(8)	2.111(9)	2.135(10)	2.158(10)	2.143(17)	2.140(6)
N(11)–C(11)	1.131(12)	1.117(12)	1.124(15)	1.140(20)	1.140(20)	1.117(9)
N(21)–C(21)	1.146(11)	1.092(12)	1.136(15)	1.135(29)	1.167(35)	1.135(9)
C(11)–S(11)	1.587(12)	1.620(13)	1.596(15)	1.596(16)	1.598(17)	1.607(9)
C(21)–S(21)	1.581(11)	1.618(12)	1.606(15)	1.580(24)	1.515(28)	1.684(10)
N(12)–C(12)	1.132(12)	1.069(12)	1.120(15)	1.134(18)	1.128(20)	1.099(10)
N(22)–C(22)	1.130(11)	1.082(14)	1.156(15)	1.136(30)	1.126(34)	1.122(10)
C(12)–S(12)	1.606(12)	1.600(12)	1.614(15)	1.629(15)	1.575(16)	1.684(10)
C(22)–S(22)	1.621(12)	1.616(14)	1.602(15)	1.634(24)	1.595(28)	1.649(11)
N(111)–C(112)	1.364(11)	1.366(12)	1.368(15)	1.339(29)	1.335(19)	1.346(8)
N(111)–C(116)	1.330(11)	1.356(13)	1.338(16)	1.325(31)	1.305(34)	1.363(9)
C(112)–C(113)	1.383(12)	1.381(13)	1.374(17)	1.393(19)	1.375(37)	1.415(10)
C(113)–C(114)	1.352(12)	1.358(14)	1.389(18)	1.389(34)	1.351(37)	1.416(11)
C(114)–C(115)	1.398(12)	1.361(14)	1.389(18)	1.385(33)	1.384(22)	1.385(10)
C(114)–C(117)	1.480(13)	1.538(16)	1.527(19)	1.574(21)	1.606(43)	1.520(11)
C(115)–C(116)	1.348(12)	1.399(15)	1.356(17)	1.411(20)	1.456(41)	1.357(10)
C(117)–C(118)	1.521(14)	1.458(17)	1.469(21)	1.518(38)	1.462(28)	1.480(12)
N(121)–C(122)	1.347(11)	1.326(12)	1.377(15)	1.380(17)	1.354(22)	1.328(8)
N(121)–C(126)	1.344(11)	1.348(12)	1.337(16)	1.318(29)	1.337(19)	1.365(10)
C(122)–C(123)	1.356(12)	1.387(15)	1.376(17)	1.377(34)	1.424(26)	1.410(9)
C(123)–C(124)	1.349(13)	1.395(16)	1.388(18)	1.370(34)	1.383(24)	1.397(11)
C(124)–C(125)	1.388(13)	1.375(16)	1.380(17)	1.379(20)	1.364(23)	1.356(10)
C(124)–C(127)	1.560(14)	1.665(22)	1.529(20)	1.552(39)	1.538(24)	1.491(11)
C(125)–C(126)	1.409(13)	1.371(15)	1.388(17)	1.354(33)	1.416(22)	1.373(10)
C(127)–C(128)	1.437(15)	1.221(26)	1.467(21)	1.536(25)	1.408(40)	1.506(12)
N(131)–C(132)	1.335(11)	1.326(12)	1.340(17)	1.271(19)	1.346(36)	1.348(10)

Table 11 (*continued*)

	(1)	(2)	(4)	(5)	(6)	(7)
N(131)–C(136)	1.358(11)	1.346(13)	1.323(16)	1.327(17)	1.312(21)	1.338(9)
C(132)–C(133)	1.382(13)	1.405(15)	1.425(20)	1.453(23)	1.443(47)	1.406(12)
C(133)–C(134)	1.386(14)	1.393(15)	1.384(19)	1.355(22)	1.331(26)	1.323(11)
C(134)–C(135)	1.405(15)	1.341(14)	1.370(18)	1.320(21)	1.386(39)	1.414(11)
C(134)–C(137)	1.601(16)	1.614(18)	1.530(20)	1.554(23)	1.517(48)	1.505(12)
C(135)–C(136)	1.373(13)	1.382(14)	1.383(18)	1.388(20)	1.390(41)	1.427(11)
C(137)–C(138)	1.304(17)	1.356(22)	1.434(21)	1.370(36)	1.467(31)	1.461(12)
N(141)–C(142)	1.351(12)	1.325(12)	1.340(17)	1.328(31)	1.312(30)	1.344(10)
N(141)–C(146)	1.350(11)	1.342(14)	1.322(16)	1.312(18)	1.284(33)	1.341(9)
C(142)–C(143)	1.363(14)	1.391(13)	1.426(20)	1.381(40)	1.387(20)	1.410(11)
C(143)–C(144)	1.437(14)	1.358(14)	1.355(19)	1.384(22)	1.343(37)	1.304(11)
C(144)–C(145)	1.363(14)	1.419(14)	1.307(18)	1.334(33)	1.377(36)	1.350(11)
C(144)–C(147)	1.583(16)	1.498(16)	1.533(20)	1.551(40)	1.543(23)	1.546(12)
C(145)–C(146)	1.355(13)	1.350(15)	1.367(18)	1.395(37)	1.440(22)	1.417(11)
C(147)–C(148)	1.245(18)	1.437(18)	1.451(21)	1.409(32)	1.490(42)	1.483(13)
N(211)–C(212)	1.324(12)	1.333(12)	1.362(15)	1.346(29)	1.313(18)	1.348(9)
N(211)–C(216)	1.334(10)	1.341(12)	1.332(15)	1.309(16)	1.330(18)	1.340(8)
C(212)–C(213)	1.401(13)	1.400(14)	1.385(17)	1.379(31)	1.394(21)	1.358(10)
C(213)–C(214)	1.377(13)	1.326(14)	1.357(18)	1.392(19)	1.369(21)	1.417(10)
C(214)–C(215)	1.372(13)	1.373(14)	1.384(18)	1.412(35)	1.349(22)	1.375(10)
C(214)–C(217)	1.527(14)	1.551(16)	1.505(20)	1.583(34)	1.547(22)	1.520(11)
C(215)–C(216)	1.388(12)	1.386(14)	1.377(18)	1.381(30)	1.387(22)	1.413(9)
C(217)–C(218)	1.451(17)	1.458(17)	1.426(22)	1.457(44)	1.468(27)	1.459(12)
N(221)–C(222)	1.337(11)	1.374(13)	1.311(16)	1.298(30)	1.369(22)	1.364(10)
N(221)–C(226)	1.353(11)	1.339(12)	1.338(17)	1.345(36)	1.331(36)	1.351(10)
C(222)–C(223)	1.391(12)	1.374(15)	1.374(18)	1.400(20)	1.411(38)	1.440(12)
C(223)–C(224)	1.362(12)	1.378(15)	1.337(18)	1.354(37)	1.386(44)	1.341(12)
C(224)–C(225)	1.372(13)	1.392(15)	1.359(20)	1.400(37)	1.386(23)	1.349(11)
C(224)–C(227)	1.629(15)	1.510(18)	1.514(19)	1.567(23)	1.522(38)	1.531(12)
C(225)–C(226)	1.395(13)	1.347(14)	1.392(19)	1.380(25)	1.398(34)	1.433(11)
C(227)–C(228)	1.319(18)	1.294(27)	1.485(17)	1.399(51)	1.474(29)	1.481(12)
N(231)–C(232)	1.328(11)	1.325(14)	1.305(17)	1.381(21)	1.357(39)	1.360(10)
N(231)–C(236)	1.339(11)	1.340(15)	1.345(16)	1.326(34)	1.341(32)	1.389(10)
C(232)–C(233)	1.379(12)	1.390(14)	1.431(20)	1.452(36)	1.384(27)	1.391(12)
C(233)–C(234)	1.365(12)	1.340(15)	1.390(21)	1.373(42)	1.370(39)	1.368(12)
C(234)–C(235)	1.369(12)	1.356(16)	1.365(19)	1.363(22)	1.363(40)	1.357(11)
C(234)–C(237)	1.508(13)	1.630(16)	1.564(20)	1.542(36)	1.531(26)	1.508(12)
C(235)–C(236)	1.384(13)	1.401(16)	1.353(18)	1.360(32)	1.368(23)	1.428(11)
C(237)–C(238)	1.510(15)	1.342(22)	1.463(21)	1.485(28)	1.449(55)	1.509(13)
N(241)–C(242)	1.337(11)	1.377(13)	1.369(15)	1.346(16)	1.336(33)	1.335(8)
N(241)–C(246)	1.352(11)	1.355(13)	1.328(15)	1.333(16)	1.272(19)	1.352(8)
C(242)–C(243)	1.384(13)	1.339(14)	1.364(17)	1.402(19)	1.360(36)	1.417(9)
C(243)–C(244)	1.360(14)	1.380(16)	1.380(18)	1.403(19)	1.401(22)	1.342(10)
C(244)–C(245)	1.394(14)	1.333(14)	1.389(17)	1.379(20)	1.337(38)	1.410(10)
C(244)–C(247)	1.585(17)	1.540(19)	1.516(19)	1.568(20)	1.541(35)	1.543(11)
C(245)–C(246)	1.340(13)	1.354(13)	1.394(17)	1.383(19)	1.437(35)	1.354(9)
C(247)–C(248)	1.270(17)	1.103(26)	1.478(21)	1.481(26)	1.509(50)	1.538(12)

For the guest molecules

	(4)
C(G11)–C(G12)	1.442(22)
C(G11)–C(G14)	1.487(25)
C(G12)–C(G13)	1.362(21)
C(G21)–C(G22)	1.380(22)
C(G21)–C(G24)	1.509(24)
C(G22)–C(G23)	1.346(20)
C(G31)–C(G32)	1.472(22)
C(G31)–C(G34)	1.510(25)
C(G32)–C(G33)	1.312(20)
C(G41)–C(G42)	1.351(21)
C(G42)–C(G43)	1.426(22)
C(G43)–C(G44)	1.521(25)

	(7)
C(G1)–S(G11)	1.527(13)
C(G1)–S(G12)	1.543(13)
C(G2)–S(G21)	1.542(13)
C(G2)–S(G22)	1.549(13)
C(G3)–S(G31)	1.547(14)
C(G3)–S(G32)	1.546(14)
C(G4)–S(G41)	1.576(14)
C(G4)–S(G42)	1.529(14)

	(5)	(6)
C(G11)–C(G12)	1.372(17)	1.408(20)
C(G11)–C(G16)	1.403(19)	1.426(18)
C(G11)–C(G17)	1.388(18)	1.402(16)
C(G12)–C(G13)	1.396(16)	1.413(21)
C(G13)–C(G14)	1.465(28)	1.398(17)
C(G13)–C(G18)	1.411(16)	1.416(16)
C(G14)–C(G15)	1.394(16)	1.392(16)
C(G15)–C(G16)	1.441(20)	1.386(18)
C(G21)–C(G22)	1.400(15)	1.403(21)
C(G21)–C(G26)	1.467(26)	1.455(31)
C(G21)–C(G27)	1.394(16)	1.433(25)
C(G22)–C(G23)	1.374(17)	1.383(17)
C(G23)–C(G24)	1.398(17)	1.397(17)
C(G23)–C(G28)	1.406(17)	1.391(15)
C(G24)–C(G25)	1.411(19)	1.401(19)
C(G25)–C(G26)	1.386(19)	1.525(38)

	(5)	(6)
C(G31)–C(G32)	1.418(27)	1.415(25)
C(G31)–C(G36)	1.455(28)	1.451(33)
C(G31)–C(G37)	1.431(23)	1.444(36)
C(G32)–C(G33)	1.462(27)	1.461(25)
C(G33)–C(G34)	1.411(26)	1.390(19)
C(G33)–C(G38)	1.393(20)	1.430(28)
C(G34)–C(G35)	1.366(23)	1.398(21)
C(G35)–C(G36)	1.468(31)	1.387(24)
C(G41)–C(G42)	1.390(15)	1.433(20)
C(G41)–C(G46)	1.388(17)	1.395(24)
C(G41)–C(G47)	1.411(17)	1.409(17)
C(G42)–C(G43)	1.409(16)	1.469(24)
C(G43)–C(G44)	1.439(17)	1.407(19)
C(G43)–C(G48)	1.380(18)	1.388(20)
C(G44)–C(G45)	1.362(16)	1.379(16)
C(G45)–C(G46)	1.386(17)	1.381(18)

Table 12. Bond distances (Å) of compounds (**3**) and (**8**)

	(3)	(8)		(3)	(8)
Ni(1)–N(1)	2.080(3)	2.065(5)	Ni(1)–N(11)	2.140(3)	2.165(4)
Ni(1)–N(21)	2.130(3)	2.142(5)	N(1)–C(1)	1.141(5)	1.150(7)
C(1)–S(1)	1.620(4)	1.623(6)	N(11)–C(12)	1.324(5)	1.332(7)
N(11)–C(16)	1.340(5)	1.345(7)	C(12)–C(13)	1.392(6)	1.387(8)
C(13)–C(14)	1.366(6)	1.387(8)	C(14)–C(15)	1.391(6)	1.359(8)
C(14)–C(17)	1.535(7)	1.515(8)	C(15)–C(16)	1.382(6)	1.370(7)
C(17)–C(18)	1.449(8)	1.465(11)	N(21)–C(22)	1.346(5)	1.337(7)
N(21)–C(26)	1.331(5)	1.334(7)	C(22)–C(23)	1.374(5)	1.382(8)
C(23)–C(24)	1.386(5)	1.381(8)	C(24)–C(25)	1.372(5)	1.382(8)
C(24)–C(27)	1.506(5)	1.514(8)	C(25)–C(26)	1.379(5)	1.382(8)
C(27)–C(28)	1.475(6)	1.481(10)			
C(G1)–Cl(G1)	1.712(3)	1.765(8)	C(G1)–Cl(G2)	1.895(10)	1.740(8)
C(G1)–Cl(G3)		1.735(8)	C(G1)–Cl(G4)		1.749(8)

Table 13. Bond angles (°) with e.s.d.s in parentheses for compounds (**1**), (**2**), and (**4**)—(**7**)

	(1)	(2)	(4)	(5)	(6)	(7)
N(111)–Ni(1)–N(11)	89.4(0.3)	89.7(0.4)	89.4(0.4)	90.0(0.5)	91.5(7)	89.9(0.2)
N(121)–Ni(1)–N(11)	90.3(0.3)	90.5(0.4)	87.8(0.4)	88.5(0.7)	90.9(0.5)	88.1(0.2)
N(121)–Ni(1)–N(111)	90.3(0.3)	90.5(0.3)	88.5(0.4)	90.5(0.5)	90.5(0.6)	89.0(0.2)
N(12)–Ni(1)–N(11)	178.0(0.4)	177.9(0.4)	176.8(0.5)	177.1(0.6)	176.4(0.6)	177.4(0.2)
N(12)–Ni(1)–N(111)	88.5(0.3)	88.4(0.3)	88.4(0.4)	88.1(0.5)	86.1(0.6)	88.7(0.2)
N(12)–Ni(1)–N(121)	89.9(0.3)	90.4(0.3)	89.9(0.4)	89.3(0.6)	91.9(0.6)	89.6(0.2)
N(131)–Ni(1)–N(11)	89.4(0.3)	91.7(0.4)	93.8(0.4)	92.8(0.5)	91.6(0.6)	92.8(0.2)
N(131)–Ni(1)–N(111)	90.2(0.3)	89.2(0.3)	92.7(0.4)	90.0(0.6)	89.2(0.6)	90.7(0.2)
N(131)–Ni(1)–N(121)	179.4(0.4)	178.6(0.3)	176.6(0.4)	177.2(0.6)	176.9(0.3)	177.3(0.2)
N(131)–Ni(1)–N(12)	90.5(0.3)	90.2(0.4)	88.5(0.4)	89.2(0.5)	90.8(0.7)	88.6(0.2)
N(141)–Ni(1)–N(11)	91.8(0.3)	89.9(0.4)	89.7(0.4)	90.0(0.7)	85.8(0.6)	89.1(0.2)
N(141)–Ni(1)–N(111)	178.4(0.3)	179.4(0.3)	177.4(0.4)	177.7(0.6)	176.5(0.6)	177.2(0.2)
N(141)–Ni(1)–N(121)	90.7(0.3)	89.8(0.3)	91.9(0.4)	91.3(0.6)	90.6(0.6)	90.5(0.2)
N(141)–Ni(1)–N(12)	90.2(0.3)	89.2(0.4)	92.6(0.4)	92.3(0.7)	91.5(0.5)	93.2(0.2)
N(141)–Ni(1)–N(131)	88.9(0.3)	90.5(0.4)	87.1(0.4)	88.2(0.7)	89.8(0.5)	89.9(0.2)
N(211)–Ni(2)–N(21)	89.8(0.3)	89.4(0.3)	86.6(0.4)	87.4(0.6)	91.8(0.6)	87.8(0.2)
N(221)–Ni(2)–N(21)	90.6(0.3)	89.2(0.4)	92.7(0.4)	92.0(0.5)	91.0(0.7)	91.9(0.3)
N(221)–Ni(2)–N(211)	90.2(0.3)	90.5(0.3)	92.7(0.4)	89.9(0.6)	91.0(0.7)	90.9(0.2)
N(22)–Ni(2)–N(21)	178.3(0.3)	178.5(0.4)	176.3(0.4)	176.3(0.7)	176.7(0.7)	177.1(0.3)
N(22)–Ni(2)–N(211)	91.7(0.3)	89.8(0.4)	90.9(0.4)	89.4(0.6)	86.0(0.5)	90.2(0.2)
N(22)–Ni(2)–N(221)	89.9(0.3)	89.5(0.4)	90.1(0.4)	89.7(0.7)	91.5(0.8)	90.2(0.3)
N(231)–Ni(2)–N(21)	88.3(0.3)	89.5(0.4)	89.9(0.4)	90.8(0.6)	91.9(0.6)	89.6(0.3)
N(231)–Ni(2)–N(211)	178.1(0.3)	177.4(0.4)	176.4(0.4)	177.9(0.5)	176.1(0.6)	177.4(0.2)
N(231)–Ni(2)–N(221)	89.7(0.3)	92.0(0.4)	86.5(0.4)	89.0(0.6)	87.8(0.7)	89.0(0.2)
N(231)–Ni(2)–N(22)	90.1(0.3)	89.5(0.4)	92.6(0.4)	92.5(0.6)	90.4(0.6)	92.4(0.3)
N(241)–Ni(2)–N(21)	90.2(0.3)	91.4(0.4)	90.5(0.4)	90.5(0.6)	86.1(0.7)	89.8(0.2)
N(241)–Ni(2)–N(211)	89.3(0.3)	88.7(0.3)	88.4(0.4)	91.2(0.5)	90.6(0.6)	88.8(0.2)
N(241)–Ni(2)–N(221)	179.9(0.3)	179.0(0.4)	176.6(0.5)	177.3(0.6)	176.7(0.5)	178.3(0.2)
N(241)–Ni(2)–N(231)	90.8(0.3)	88.7(0.4)	92.7(0.4)	90.0(0.6)	90.8(0.7)	91.3(0.2)
N(241)–Ni(2)–N(22)	89.3(0.3)	89.9(0.4)	86.7(0.4)	87.9(0.5)	91.5(0.7)	88.2(0.2)
C(11)–N(11)–Ni(1)	173.4(0.9)	156.6(1.0)	168.4(1.2)	164.6(1.4)	169.3(1.4)	159.6(0.7)
N(11)–C(11)–S(11)	178.3(1.1)	176.5(1.2)	179.3(1.4)	179.6(2.0)	178.8(1.6)	178.3(0.8)
C(12)–N(12)–Ni(1)	175.2(0.9)	164.0(1.0)	168.0(1.2)	164.0(1.4)	167.3(1.5)	158.7(0.7)
N(12)–C(12)–S(12)	177.3(1.1)	177.0(1.2)	179.5(1.2)	179.1(1.6)	178.1(1.7)	179.5(0.7)
C(112)–N(111)–Ni(1)	119.2(0.8)	121.8(0.8)	119.8(0.9)	118.9(1.1)	122.4(1.3)	119.6(0.5)
C(116)–N(111)–Ni(1)	121.9(0.8)	124.5(0.8)	124.4(0.9)	122.3(1.2)	124.2(1.3)	123.5(0.5)
C(116)–N(111)–C(112)	116.1(1.0)	116.3(1.0)	115.8(1.2)	118.8(1.5)	113.4(1.7)	116.9(0.7)
C(113)–C(112)–N(111)	121.5(1.1)	122.8(1.1)	123.0(1.4)	121.4(1.7)	126.1(1.7)	122.9(0.7)
C(114)–C(113)–C(112)	121.1(1.1)	119.6(1.2)	120.4(1.4)	119.6(1.7)	119.9(1.8)	119.0(0.8)
C(115)–C(114)–C(113)	116.8(1.1)	119.6(1.2)	115.8(1.4)	119.4(1.6)	118.7(1.9)	116.1(0.8)
C(117)–C(114)–C(113)	122.4(1.1)	123.3(1.2)	122.3(1.4)	124.2(1.7)	125.3(1.7)	120.7(0.7)
C(117)–C(114)–C(115)	120.7(1.1)	117.1(1.2)	122.0(1.4)	116.4(1.7)	115.9(1.7)	123.2(0.8)
C(116)–C(115)–C(114)	119.5(1.1)	119.3(1.3)	121.3(1.5)	116.8(1.7)	115.5(1.7)	122.1(0.8)
C(115)–C(116)–N(111)	124.8(1.1)	122.4(1.2)	123.7(1.4)	123.9(1.8)	126.5(1.7)	123.0(0.8)
C(118)–C(117)–C(114)	114.5(1.0)	112.5(1.3)	115.8(1.6)	109.6(1.6)	111.9(2.1)	118.4(0.8)
C(122)–N(121)–Ni(1)	123.3(0.8)	121.8(0.8)	119.6(0.9)	118.1(1.2)	119.7(1.4)	120.1(0.5)
C(126)–N(121)–Ni(1)	121.5(0.8)	120.5(0.8)	123.4(0.9)	124.0(1.3)	122.6(1.1)	122.7(0.5)
C(126)–N(121)–C(122)	115.2(1.0)	117.5(1.0)	117.0(1.2)	117.9(1.7)	117.5(1.6)	117.2(0.6)
C(123)–C(122)–N(121)	125.3(1.1)	122.2(1.2)	121.5(1.4)	120.4(1.5)	124.6(2.2)	122.8(0.7)
C(124)–C(123)–C(122)	119.1(1.2)	120.9(1.3)	121.4(1.4)	121.0(1.8)	116.0(2.0)	119.3(0.7)
C(125)–C(124)–C(123)	119.3(1.2)	115.4(1.4)	116.4(1.4)	116.7(2.0)	120.0(2.0)	116.7(0.8)
C(127)–C(124)–C(123)	123.7(1.2)	119.4(1.5)	123.9(1.4)	123.7(1.7)	116.8(1.9)	121.4(0.7)

Table 13 (*continued*)

	(1)	(2)	(4)	(5)	(6)	(7)
C(127)–C(124)–C(125)	117.0(1.1)	124.6(1.5)	119.6(1.4)	119.5(1.6)	123.2(2.0)	121.8(0.8)
C(126)–C(125)–C(124)	117.8(1.1)	121.4(1.4)	120.6(1.4)	121.1(1.6)	120.8(2.0)	122.1(0.8)
C(125)–C(126)–N(121)	123.1(1.1)	122.5(1.2)	123.0(1.3)	122.8(1.6)	119.2(2.1)	121.9(0.8)
C(128)–C(127)–C(124)	113.8(1.2)	93.7(1.8)	113.8(1.5)	112.1(1.9)	113.9(1.9)	116.6(0.8)
C(132)–N(131)–Ni(1)	122.5(0.8)	120.3(0.8)	122.1(1.0)	120.5(1.3)	121.7(1.4)	119.8(0.5)
C(136)–N(131)–Ni(1)	121.0(0.8)	121.2(0.8)	124.8(1.0)	123.2(1.1)	124.1(1.7)	123.2(0.5)
C(136)–N(131)–C(132)	116.5(1.0)	118.3(1.1)	113.0(1.3)	116.3(1.5)	114.1(2.1)	116.9(0.7)
C(133)–C(132)–N(131)	123.7(1.1)	122.2(1.2)	125.5(1.5)	124.6(2.0)	126.4(2.3)	123.0(0.9)
C(134)–C(133)–C(132)	118.6(1.2)	118.4(1.3)	118.4(1.6)	117.0(1.9)	115.6(2.6)	120.8(0.9)
C(135)–C(134)–C(133)	119.4(1.3)	118.4(1.4)	115.8(1.5)	117.9(1.8)	119.9(2.3)	118.5(0.8)
C(137)–C(134)–C(133)	118.4(1.3)	115.5(1.3)	120.3(1.5)	120.9(1.8)	116.4(2.5)	121.4(0.8)
C(137)–C(134)–C(135)	122.2(1.3)	125.4(1.3)	123.9(1.4)	121.1(1.9)	123.7(2.3)	120.2(0.8)
C(136)–C(135)–C(134)	177.1(1.3)	120.9(1.3)	121.1(1.5)	121.6(1.9)	119.6(2.2)	118.1(0.8)
C(135)–C(136)–N(131)	124.7(1.2)	121.7(1.2)	125.9(1.5)	122.6(1.7)	124.4(2.3)	122.7(0.8)
C(138)–C(137)–C(134)	115.5(1.4)	102.0(1.5)	113.6(1.6)	113.5(2.1)	111.1(2.1)	115.0(0.9)
C(142)–N(141)–Ni(1)	120.6(0.8)	121.2(0.8)	121.1(1.0)	120.6(1.5)	120.3(1.1)	120.4(0.6)
C(146)–N(141)–Ni(1)	122.4(0.8)	122.4(0.9)	126.2(1.0)	122.5(1.4)	122.7(1.6)	123.4(0.6)
C(146)–N(141)–C(142)	116.9(1.0)	116.4(1.1)	112.7(1.3)	116.9(2.0)	116.7(1.7)	116.1(0.7)
C(143)–C(142)–N(141)	123.1(1.2)	123.7(1.1)	123.7(1.5)	123.9(2.0)	123.8(1.9)	118.4(0.5)
C(144)–C(143)–C(142)	119.3(1.2)	119.9(1.2)	118.5(1.6)	119.6(2.1)	120.9(2.2)	123.2(0.8)
C(145)–C(144)–C(143)	116.0(1.2)	116.4(1.2)	117.9(1.5)	115.0(2.2)	116.4(1.8)	118.7(0.9)
C(147)–C(144)–C(143)	116.8(1.2)	123.3(1.2)	118.7(1.5)	123.1(1.8)	126.2(2.3)	121.4(0.9)
C(147)–C(144)–C(145)	126.9(1.3)	120.2(1.2)	123.4(1.4)	121.8(1.9)	117.4(2.0)	118.3(0.9)
C(146)–C(145)–C(144)	121.7(1.2)	119.7(1.3)	120.9(1.5)	123.5(1.9)	118.6(2.0)	120.3(0.9)
C(145)–C(146)–N(141)	123.0(1.1)	123.8(1.3)	126.2(1.5)	120.9(1.8)	123.5(2.2)	118.4(0.9)
C(148)–C(147)–C(144)	107.5(1.5)	113.7(1.3)	110.8(1.5)	113.6(2.3)	110.7(1.8)	122.1(0.8)
C(21)–N(21)–Ni(2)	165.7(0.9)	171.0(1.0)	168.1(1.1)	166.5(1.4)	166.7(1.7)	162.1(0.8)
N(21)–C(21)–S(21)	179.7(0.6)	179.0(1.1)	178.2(1.4)	179.5(1.8)	178.3(2.3)	177.3(0.9)
C(22)–N(22)–Ni(2)	154.5(0.9)	171.3(1.1)	167.6(1.2)	162.8(1.5)	167.5(1.8)	161.4(0.8)
N(22)–C(22)–S(22)	178.5(1.1)	178.2(1.3)	179.0(1.4)	177.1(1.7)	179.5(2.3)	178.1(0.9)
C(212)–N(211)–Ni(2)	120.2(0.8)	119.8(0.8)	121.3(0.9)	119.1(1.2)	120.3(1.3)	122.9(0.5)
C(216)–N(211)–Ni(2)	122.1(0.7)	122.6(0.8)	123.8(0.9)	122.4(1.4)	122.6(1.2)	119.8(0.5)
C(216)–N(211)–C(212)	117.6(1.0)	117.4(1.0)	114.9(1.2)	118.4(1.6)	116.6(1.5)	117.3(0.6)
C(213)–C(212)–N(211)	123.7(1.2)	122.7(1.2)	123.7(1.3)	123.6(1.9)	122.6(1.8)	123.6(0.7)
C(214)–C(213)–C(212)	117.7(1.2)	118.2(1.2)	121.4(1.4)	118.5(2.0)	121.3(1.7)	120.0(0.8)
C(215)–C(214)–C(213)	119.0(1.2)	121.3(1.3)	114.5(1.4)	117.1(1.8)	115.0(1.8)	116.8(0.7)
C(217)–C(214)–C(213)	122.3(1.2)	119.6(1.2)	124.6(1.4)	123.5(2.1)	123.7(1.7)	120.8(0.7)
C(217)–C(214)–C(215)	118.6(1.2)	119.0(1.2)	120.9(1.4)	119.3(1.9)	121.4(1.9)	122.4(0.7)
C(216)–C(215)–C(214)	119.3(1.2)	117.6(1.2)	122.6(1.4)	119.8(1.9)	122.0(2.0)	119.8(0.7)
C(215)–C(216)–N(211)	122.6(1.1)	122.7(1.1)	122.8(1.4)	122.6(2.0)	122.3(1.8)	122.5(0.6)
C(218)–C(217)–C(214)	113.1(1.2)	113.3(1.3)	113.3(1.5)	111.2(1.8)	114.0(1.9)	116.4(0.8)
C(222)–N(221)–Ni(2)	121.4(0.7)	121.3(0.8)	124.2(1.0)	122.4(1.6)	119.6(1.5)	119.3(0.6)
C(226)–N(221)–Ni(2)	120.8(0.7)	122.8(0.8)	120.4(1.0)	119.6(1.2)	122.9(1.3)	124.1(0.6)
C(226)–N(221)–C(222)	117.4(0.9)	115.8(1.0)	115.3(1.3)	117.9(1.8)	117.5(2.0)	116.5(0.7)
C(223)–C(222)–N(221)	123.0(1.0)	121.9(1.2)	125.2(1.5)	122.5(2.0)	124.1(2.0)	120.7(0.9)
C(224)–C(223)–C(222)	118.9(1.1)	121.2(1.4)	118.3(1.5)	119.6(1.7)	117.3(2.1)	121.8(0.9)
C(225)–C(224)–C(223)	119.6(1.1)	117.2(1.3)	119.7(1.5)	119.2(2.1)	118.1(2.4)	117.9(0.9)
C(227)–C(224)–C(223)	126.1(1.1)	125.9(1.4)	116.4(1.4)	120.6(1.9)	116.9(1.9)	119.2(0.2)
C(227)–C(224)–C(225)	113.7(1.1)	116.9(1.4)	123.8(1.5)	120.2(2.1)	125.0(2.0)	122.9(0.9)
C(226)–C(225)–C(224)	118.8(1.1)	118.7(1.3)	118.1(1.6)	116.7(2.3)	121.7(1.9)	120.4(0.9)
C(225)–C(226)–N(221)	122.2(1.0)	125.0(1.2)	123.3(1.6)	124.1(2.1)	121.2(1.7)	122.6(0.8)
C(228)–C(227)–C(224)	102.1(1.4)	111.8(1.9)	106.2(1.3)	117.2(2.0)	112.0(2.4)	113.1(0.9)
C(232)–N(231)–Ni(2)	121.8(0.8)	125.3(0.9)	119.3(1.1)	117.5(1.3)	119.9(1.3)	120.0(0.6)
C(236)–N(231)–Ni(2)	123.6(0.8)	119.6(1.0)	123.4(1.0)	123.8(1.2)	122.7(1.4)	123.3(0.5)
C(236)–N(231)–C(232)	114.5(0.9)	115.1(1.2)	117.3(1.3)	118.7(1.7)	117.4(1.7)	116.7(0.7)
C(233)–C(232)–N(231)	125.2(1.1)	124.0(1.3)	121.9(1.6)	118.7(1.7)	123.2(2.1)	122.4(1.0)
C(234)–C(233)–C(232)	119.1(1.1)	121.2(1.3)	118.5(1.7)	120.7(1.9)	117.2(2.2)	121.3(0.9)
C(235)–C(234)–C(233)	117.4(1.1)	115.7(1.3)	117.8(1.6)	116.3(2.0)	120.5(1.9)	118.3(0.9)
C(237)–C(234)–C(233)	122.6(1.1)	131.7(1.2)	119.9(1.5)	120.6(1.8)	116.4(2.0)	120.9(0.9)
C(237)–C(234)–C(235)	119.7(1.1)	112.5(1.2)	122.3(1.5)	123.1(1.8)	123.0(1.9)	120.8(0.9)
C(236)–C(235)–C(234)	119.5(1.1)	121.4(1.5)	119.6(1.6)	123.3(1.8)	119.5(1.9)	120.5(0.9)
C(235)–C(236)–N(231)	124.1(1.1)	122.3(1.5)	124.5(1.5)	122.3(1.7)	122.2(1.9)	120.8(0.8)
C(238)–C(237)–C(234)	112.8(1.1)	104.9(1.5)	114.0(1.5)	122.9(1.8)	116.6(2.3)	114.3(0.9)
C(242)–N(241)–Ni(2)	121.9(0.8)	122.1(0.8)	120.7(0.9)	117.7(1.1)	120.5(1.4)	118.9(0.5)
C(246)–N(241)–Ni(2)	121.3(0.7)	122.7(0.8)	122.7(0.9)	122.5(1.0)	122.9(1.5)	123.3(0.5)
C(246)–N(241)–C(242)	116.8(1.0)	115.1(1.0)	116.6(1.2)	119.6(1.4)	116.5(2.0)	117.8(0.6)
C(243)–C(242)–N(241)	122.0(1.1)	121.9(1.2)	123.2(1.3)	120.5(1.6)	123.4(1.9)	121.1(0.7)
C(244)–C(243)–C(242)	120.1(1.2)	121.3(1.3)	121.1(1.4)	119.6(1.5)	120.2(2.2)	120.7(0.7)
C(245)–C(244)–C(243)	117.9(1.3)	117.4(1.3)	115.5(1.4)	118.1(1.8)	116.7(2.3)	117.5(0.7)
C(247)–C(244)–C(243)	123.4(1.3)	124.8(1.4)	124.5(1.4)	122.2(1.6)	126.1(2.0)	123.5(0.7)
C(247)–C(244)–C(245)	118.7(1.3)	117.8(1.4)	120.0(1.3)	119.7(1.7)	117.2(2.0)	118.9(0.7)
C(246)–C(245)–C(244)	119.0(1.2)	120.8(1.3)	121.4(1.4)	119.3(1.7)	118.6(2.0)	119.6(0.7)

Table 13 (*continued*)

	(1)	(2)	(4)	(5)	(6)	(7)
C(245)–C(246)–N(241)	116.9(0.6)	123.5(1.2)	122.2(1.3)	122.8(1.5)	124.6(2.0)	123.2(0.7)
C(248)–C(247)–C(244)	121.7(1.6)	123.9(2.5)	112.9(1.5)	109.5(1.9)	110.9(2.1)	114.5(0.8)

In the guest molecules

	(4)		(5)	(6)		(5)	(6)
C(G14)–C(G11)–C(G12)	125.5(1.9)	C(G16)–C(G11)–C(G12)	120.9(1.2)	119.7(1.5)	C(G36)–C(G31)–C(G32)	120.8(2.1)	122.4(1.3)
C(G13)–C(G12)–C(G11)	125.2(1.7)	C(G17)–C(G11)–C(G12)	118.3(1.9)	118.4(2.0)	C(G37)–C(G31)–C(G32)	118.4(1.6)	122.3(1.6)
C(G24)–C(G21)–C(G22)	124.3(1.9)	C(G17)–C(G11)–C(G16)	120.4(1.5)	118.3(1.5)	C(G37)–C(G31)–C(G36)	118.6(1.6)	115.2(1.6)
C(G23)–C(G22)–C(G21)	124.6(1.8)	C(G13)–C(G12)–C(G11)	119.4(1.4)	116.3(1.9)	C(G33)–C(G32)–C(G31)	113.6(2.4)	116.0(2.0)
C(G34)–C(G31)–C(G33)	119.1(1.8)	C(G14)–C(G13)–C(G12)	120.5(1.5)	121.0(1.3)	C(G34)–C(G33)–C(G32)	122.9(1.4)	120.0(1.6)
C(G32)–C(G33)–C(G31)	120.4(1.6)	C(G18)–C(G13)–C(G12)	114.6(1.7)	118.1(1.8)	C(G38)–C(G33)–C(G32)	117.0(1.7)	121.2(2.0)
C(G44)–C(G43)–C(G42)	124.3(1.9)	C(G18)–C(G13)–C(G14)	115.0(2.2)	119.6(1.5)	C(G38)–C(G33)–C(G34)	119.1(2.6)	116.7(2.3)
C(G43)–C(G42)–C(G41)	123.8(1.7)	C(G15)–C(G14)–C(G13)	118.5(2.0)	119.5(1.4)	C(G35)–C(G34)–C(G33)	117.8(2.7)	119.8(1.4)
		C(G16)–C(G15)–C(G14)	117.1(1.3)	120.6(1.3)	C(G36)–C(G35)–C(G34)	123.0(1.9)	121.5(1.7)
	(7)	C(G15)–C(G16)–C(G11)	121.4(1.3)	118.9(1.2)	C(G35)–C(G36)–C(G31)	112.7(2.5)	116.1(2.8)
S(G12)–C(G1)–S(G11)	169.1(0.9)	C(G26)–C(G21)–C(G22)	119.2(1.8)	122.1(1.4)	C(G46)–C(G41)–C(G42)	121.9(1.3)	123.4(1.5)
S(G22)–C(G2)–S(G21)	170.4(1.0)	C(G27)–C(G21)–C(G22)	117.4(1.7)	114.5(2.4)	C(G47)–C(G41)–C(G42)	119.5(1.8)	116.6(1.7)
S(G32)–C(G3)–S(G31)	169.9(1.0)	C(G27)–C(G21)–C(G26)	116.0(2.2)	123.4(1.7)	C(G47)–C(G41)–C(G46)	118.0(1.7)	118.3(2.2)
S(G42)–C(G4)–S(G41)	172.0(1.0)	C(G23)–C(G22)–C(G21)	118.6(1.3)	119.5(1.7)	C(G43)–C(G42)–C(G41)	117.3(1.3)	112.8(1.6)
		C(G24)–C(G23)–C(G22)	122.3(1.2)	122.7(1.5)	C(G44)–C(G43)–C(G42)	121.2(1.3)	123.3(1.1)
		C(G28)–C(G23)–C(G22)	119.3(1.6)	117.9(1.6)	C(G48)–C(G43)–C(G42)	120.4(1.9)	117.8(1.6)
		C(G28)–C(G23)–C(G24)	118.1(1.6)	119.1(1.6)	C(G48)–C(G43)–C(G44)	116.4(2.0)	118.6(2.1)
		C(G25)–C(G24)–C(G23)	119.1(1.6)	119.4(1.4)	C(G45)–C(G44)–C(G43)	117.4(1.3)	118.7(1.3)
		C(G26)–C(G25)–C(G24)	120.1(1.4)	118.8(2.2)	C(G46)–C(G45)–C(G44)	122.5(1.4)	121.7(1.5)
		C(G25)–C(G26)–C(G21)	118.5(1.3)	113.6(2.4)	C(G45)–C(G46)–C(G41)	119.2(1.2)	119.9(1.4)

Table 14. Bond angles (°) with e.s.d.s in parentheses for compounds (**3**) and (**8**)

	(3)	(8)		(3)	(8)
N(11)–Ni(1)–N(1)	90.2(0.1)	90.3(0.2)	N(21)–Ni(1)–N(1)	88.7(0.1)	90.1(0.2)
N(21)–Ni(1)–N(11)	178.7(0.1)	94.1(0.2)	C(1)–N(1)–Ni(1)	153.2(0.3)	164.6(0.5)
S(1)–C(1)–N(1)	179.8(0.1)	178.4(0.6)	C(12)–N(11)–Ni(1)	119.5(0.3)	123.5(0.4)
C(16)–N(11)–Ni(1)	122.5(0.3)	119.3(0.4)	C(16)–N(11)–C(12)	117.6(0.4)	116.7(0.5)
C(13)–C(12)–N(11)	123.3(0.4)	122.8(0.6)	C(14)–C(13)–C(12)	118.8(0.5)	119.6(0.6)
C(15)–C(14)–C(13)	118.6(0.5)	117.1(0.6)	C(17)–C(14)–C(13)	119.4(0.5)	120.1(0.6)
C(17)–C(14)–C(15)	121.9(0.5)	122.8(0.6)	C(16)–C(15)–C(14)	118.7(0.5)	120.7(0.6)
C(15)–C(16)–N(11)	122.8(0.4)	123.0(0.6)	C(18)–C(17)–C(14)	110.5(0.5)	110.3(0.7)
C(22)–N(21)–Ni(1)	121.0(0.3)	119.7(0.4)	C(26)–N(21)–Ni(1)	122.4(0.3)	124.1(0.4)
C(26)–N(21)–C(22)	116.5(0.3)	116.2(0.6)	C(23)–C(22)–N(21)	123.1(0.4)	123.3(0.6)
C(24)–C(23)–C(22)	120.3(0.4)	119.7(0.6)	C(25)–C(24)–C(23)	116.2(0.4)	117.8(0.7)
C(27)–C(24)–C(23)	123.0(0.4)	121.2(0.6)	C(27)–C(24)–C(25)	120.8(0.4)	121.0(0.6)
C(26)–C(25)–C(24)	120.8(0.4)	118.5(0.7)	C(25)–C(26)–N(21)	118.3(0.2)	124.5(0.6)
C(28)–C(27)–C(24)	115.3(0.4)	112.9(0.7)	Cl(G1)–C(G1)–Cl(G2)		108.3(0.4)
Cl(G3)–C(G1)–Cl(G1)		109.2(0.5)	Cl(G4)–C(G1)–Cl(G1)		108.9(0.4)
Cl(G3)–C(G1)–Cl(G2)		109.8(0.4)	Cl(G4)–C(G1)–Cl(G2)		109.1(0.5)
Cl(G4)–C(G1)–Cl(G3)		111.4(0.5)			

Table 15. Packing densities and volume comparisons

Compound	Volume per non-hydrogen atom/Å^3	Volume per guest molecule/Å^3	
(**1**)	20.8		
(**2**)	20.8		
(**3**)	21.8	141.1	1.74 × ordered CCl_4
(**4**)	20.1	133.3	
(**5**)	20.7	163.7 $V_m - V_p$ = 1.1 × ordered CH_3	
(**6**)	20.6	158.7 $V_o - V_p$ = 1.3 × ordered CH_3	
(**7**)	20.7	60.0	
(**8**)	22.2	137.8	1.79 × ordered CCl_4

distorted hour-glass shape, similar to those found in Dianin's compounds.[23] The maximum width of the channel is 16 Å, allowing two carbon tetrachloride molecules to be located on either side of the centre of inversion, Wyckoff position d. The volume available to these two guest molecules was calculated to

Table 16. Mass spectral fragmentation patterns

(*a*) The host complex $[Ni(NCS)_2(4Et\text{-}py)_4]$

Fragment *m/z*	Abundance/ %	Possible assignment
107	100	$C_7H_9N^+$
106	100	$C_7H_8N^+$
92	69	$C_6H_6N^+$
79	34	$C_5H_5N^+$
65	38	$C_5H_5^+/C_4H_3N^+$
51	25	$C_4H_3^+$
39	24	$C_3H_3^+$

(*b*) The guest molecule CCl_4

117	100	CCl_3^+
83	26	CCl_2^+
47	32	CCl^+
35	26	Cl^+

be *ca.* 304 Å^3. The constrictions in the channels lie at the centres of inversion, Wyckoff position c, and are elliptically shaped with cross-sections of *ca.* 2 and 3 Å. This is too narrow to allow free movement of guest molecules through the channel, although inspection of the projection shown in Figure 7 indicates that a simple rotation of a pyridine moiety about its Ni–N bond would ease this constricture.

Mass spectrometry was carried out for all compounds prior to data collections as part of the characterisation procedure. A typical total-ion-current spectrum of a clathrate reveals two distinct peaks as shown for compound (**8**) in Figure 8. From the fragmentation patterns, the first peak corresponds to guest breakdown and the second to the breakdown of host molecules, as listed in Table 16 for compounds (**3**) and (**8**). This illustrates the fact that the guest molecules, being held in the lattice by relatively weak non-bonded interactions, are vaporised sooner than the bonded host ligands. Figure 8 also shows the spectra of the two fragments with $m/z = 117$, to monitor guest breakdown, and $m/z = 107$, to monitor breakdown of the host molecules, superimposed on the total-ion-current spectrum for compounds (**3**) and (**8**). In compound (**8**) virtually all the guest disappears after the first ten scans. By contrast, the breakdown of compound (**3**) reveals some host breakdown in the first 13 scans followed by rapid guest removal in scans 15—25 and the bulk host breakdown in subsequent scans, thus illustrating that the guest is more strongly held in this compound.

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